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The use of palladium-catalysed cross-coupling for the synthesis of polymers incorporating vinylene and ethynylene groups

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Abstract. Methods for the synthesis of polyconjugated polyarylenevinylenes and polyaryleneethynylenes based on polycondensation catalysed by palladium complexes are reviewed. The bibliography includes 134 references.

I. Introduction

Synthesis of new π-conjugated polymers and investigation of their chemical and physical properties have attracted much attention in last decade.[1–4] In this period polyacetylene,[5] polydiacetylene[6] and numerous polyarylenes incorporating aromatic carbo- and heterocycles[7–10] have been obtained. Among these polymers, of special interest are the so-called polyarylenevinylenes (PARV) and polyaryleneethynylenes (PARE)

$$\text{–[Ar–CH=CH–]}_n\text{–} \quad \text{(PARV)} \qquad \text{–[Ar–C≡C–]}_n\text{–} \quad \text{(PARE)}$$

These polymers are distinguished by high electrical conductivity,[1,11,12] relatively high non-linear third-order optical activity[13] and electroluminescence.[14,15] Of current interest is the use of these polymers in light-emitting diodes.[16–20]

Formerly, these polymers were prepared by the Wittig reaction[21] and condensation according to McMurry.[22,23] However, due to the insolubility of polyarylenes, they are usually prepared *via* water-soluble intermediates or *via* products of the metathesis of corresponding cyclic compounds.[24–26] Both methods include the stage of thermal elimination of low-molecular-weight products, which is not quantitative. As a result, the final products are contaminated with admixtures and this results in reduced electric activity of these materials.[27,28]

Hörhold *et al.*[29,30] used dehalogenation of *p*-xylylene systems to prepare soluble phenyl-substituted PARV. However, this approach has the same disadvantages as the aforementioned two-stage methods.[24–26]

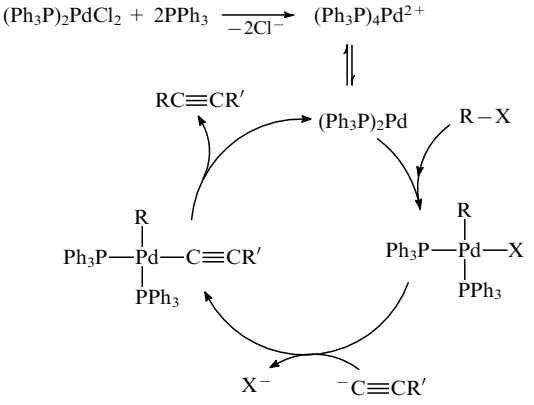
Syntheses of PARV or PARE type polymers are largely based on the studies by Heck *et al.*[31–38] and Sonogashira *et al.*[39–41] devoted to the reactions of alkenes with aliphatic or aromatic iodides or bromides in the presence of Pd^0 or Pd^{II} complexes. Usually, the reaction is performed either in the presence of 1 mol.% – 5 mol.% of palladium salt or in the presence of Pd^0 or Pd^{II} complexes with PPh_3 or other ligands, CuI as a promoter and a base (amine) that is needed to neutralise the hydrogen halide released and for the reduction of Pd^{II} to Pd^0.

$$RX + \underset{}{\overset{H}{\overset{|}{C}}=\overset{}{C}} \xrightarrow[Bu_3N]{Pd(OAc)_2} \overset{R}{\overset{|}{C}}=C + HX\,, \qquad (1)$$

$$\text{Ph–I} + HC{\equiv}CH \xrightarrow[Et_2NH,\ CuI]{PdCl_2(PPh_3)_2} \text{Ph–C}{\equiv}CH + HI\,. \qquad (2)$$

The Heck's reaction generally comprises two principal stages;[38] the first one is the formation of an organopalladium salt by oxidative addition, the second is the addition of the salt to alkene or acetylene with subsequent elimination of palladium hydride leading to the product of coupling. The selectivity of this process is determined by the reaction conditions and especially by the catalytic system. Thus when the Pd – AsR_3 system is used, two molecules of aryl halide are coupled; the yield of dimer is ~55%.[42]

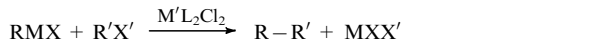
The mechanism of this process was studied in more detail using the formation of diarylacetylene as an example[43]



Reactions of organometallic compounds (Grignard reagents) with halogen-substituted organic compounds are also widely used for syntheses of PARV and PARE; these reactions are catalysed by Pd or Ni salts.[44–50]

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$M = Mg, Zn, SnBu_2$; $M' = Pd, Ni$; $L = PPh_3$;
$X, X' = Hal$; $R = Alk$, $R' = Alk, Ar$, alkenyl, alkynyl.

The mechanism of these reactions is similar to that of reactions (1) and (2). On the first stage, the Grignard reagent and palladium–(or nickel)–phosphine complex form an organopalladium (organonickel) salt, which further yields coupling products in reactions with alkyl, aryl, alkenyl or alkynyl halides.

And finally, PARV and PARE can be prepared by reactions of aryl halides with alkynyl compounds in the presence of Pd complexes and phase-transfer catalysts.[51–53]

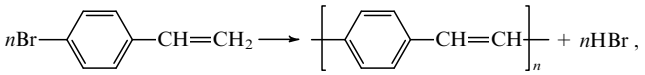
All aforementioned processes have substantial yields of by-products.[54] Hence these reactions of cross-coupling are far from ideal for polymer synthesis.[9] Nevertheless, these reactions were used at different times for the preparation of PARV and PARE.

In this decade, one-stage direct reactions of aryl halides with vinyl- or ethynyl-containing compounds, which are catalysed by complexes of transition metals, primarily palladium complexes, are mainly used for synthesis of PARV and PARE.[7–9]

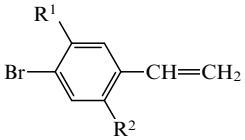
II. Synthesis of polyarylenevinylenes

The very first reports on the syntheses of PARV by Pd-catalysed cross-coupling[55–57] considered various possibilities for their implementation, namely, homopolycondensation of 4-bromostyrene,[56] reaction of *p*-divinylarenes with dihaloarenes,[55] reaction of ethylene with dihaloarenes.[57]

Homopolycondensation of 4-bromostyrene[56] according to the following scheme



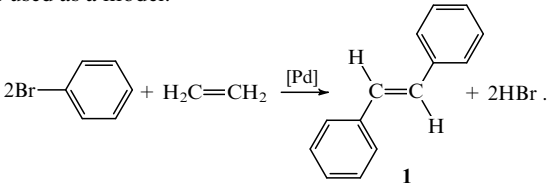
yields insoluble PARV, this predetermines its low molecular weight. It is possible in principle[57] to use in this reaction substituted 4-bromostyrenes of the general formula



$R^1 = H, R^2 = Me, Ph, CF_3$; $R^1 = R^2 = Me$,

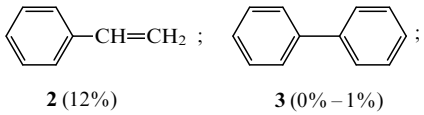
which provide a possibility of preparing polymers with improved solubility, however this synthetic procedure for PARV did not find much application.

A method based on the reaction of ethylene with dihaloarenes became more popular; this is due to the availability of the reactants. Heitz *et al.*[42, 54, 57–60] have systematically studied this reaction. The reaction of ethylene with 2 mol of bromobenzene was used as a model.

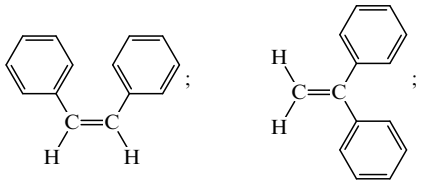


1

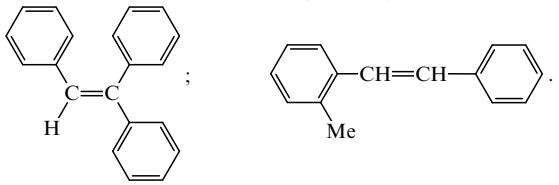
This reaction was performed in the presence of a palladium acetate–tris(*o*-tolyl)phosphine–triethylamine catalytic system. It was found that, additionally to the target *trans*-stilbene **1** (75%–95% yield), compounds **2**–**7** were also formed:



2 (12%) **3** (0%–1%)



4 (< 0.1%) **5** (3%–5%)



6 (0%–5%) **7** (0.5%–1%)

The mechanism proposed by Heck[35] explains the formation of these compounds. Styrene (**2**) is formed in side reactions of bromobenzene, when excess of ethylene is used; biphenyl **3** is formed in the arylation of bromobenzene; *cis*-stilbene **4** appears as a result of conformational transformation in the transition complex; 1,1-diphenylethylene **5** is the product of α,β-addition of intermediate Pd–aryl complex with the alkene; triphenylethylene **6** is formed upon additional arylation of stilbene; *trans*-1-phenyl-2-*o*-tolylethylene **7** is a product of the reaction of ethylene or styrene with tris(*o*-tolyl)phosphine, which is used as a cocatalyst.[54]

The side reactions of alkene with the cocatalyst and dehalogenation can result in lower molecular weight of the polymer, whereas formation of diaryls must not block the growth of macromolecules. The presence of triphenylethylene among the reaction products can result in the formation of cross-linked polymers.[54]

The yield of the target *trans*-stilbene can be maximised and the role of side reactions substantially reduced if not suppressed by variation of such factors as the nature of halide and substituents in the haloarenes, composition and quantity of the catalyst, solvent, reaction temperature, pressure of ethylene.[54]

It was shown that (a) bromoarenes are most suitable for the purpose (chloroarenes have low reactivity, whereas iodoarenes sometimes have lower selectivity of the reaction compared to bromoarenes); (b) with bromoarenes, tris(*o*-tolyl)phosphine should be added as a cocatalyst, whereas it is not necessary for iodoarenes; (c) electron-acceptor substituents in haloarenes promote the reaction, while electron-donor ones do not; (d) a lower concentration of the catalyst, palladium acetate, brings about higher yield of the target compound and lower yield of side products (with the exception of 1,1-diphenylethylene); (e) the nature of solvent [acetonitrile, methanol, DMF, *N*-methylpyrrolidone (*N*-MP), *N*-methylcaprolactam, DMSO] affects the yield of the product (the highest yield of *trans*-stilbene was attained with the use of DMF); (f) an increase in the temperature accelerates the main reaction, while selectivity becomes lower (the temperature of 50–100 °C provides the maximum yield of *trans*-stilbene); (g) lower pressures of ethylene favour formation of stilbene and higher pressures, of styrene.

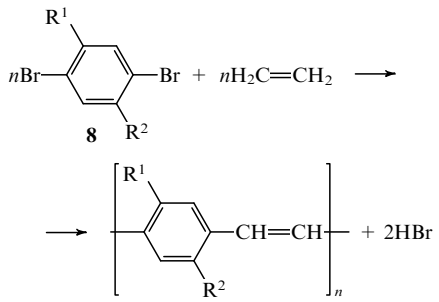
A systematic study of the reactions of non-substituted, mono-, and disubstituted *p*-dibromobenzenes **8** with ethylene, which proceed according to Scheme 1, was reported in Ref. 57.

Table 1. The weight-average molecular weights (M_w), softening temperature (T_s), decomposition temperature (T_d), and composition of PARV **9**–**13**.[57]

PARV	R^1	R^2	M_w		T_s [c] /°C	T_d /°C		Content of Br (%)	
			fraction I [a]	fraction II [b]		fraction I	fraction II	fraction I	fraction II
9	H	H	< 500	–	–	150	200	–	9.87
10	H	Me	1700	12 700	150	200	210	2.21	–
11	H	CF_3	1000	3120	175	205	238	1.15	–
12	H	Ph	8000	–	155	210	290	0.71	–
13	Me	Me	900	2600	–	190	205	–	9.87

[a] Determined by GPC with polystyrene standard. [b] Determined by GPC with poly(phenylene sulfide) standard. [c] Determined using polarisation microscope at a heating rate of 10 deg min^{-1}.

Scheme 1



8 **9**–**13**

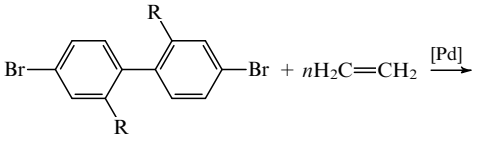
R^1 = H: R^2 = H (**9**), Me (**10**), CF_3 (**11**), Ph (**12**);
R^1 = R^2 = Me (**13**).

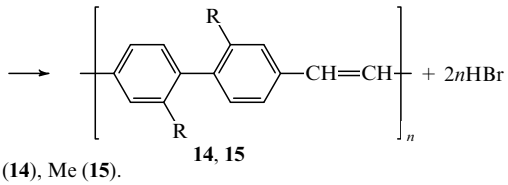
The synthesis of PARV **9**–**13** was performed in DMF with the $Pd(OAc)_2$–P(Tol-*o*)$_3$–NEt_3 catalytic system at 100 °C for 20 h. In all cases two fractions, DMF-soluble and DMF-insoluble, were isolated from the reaction mixtures. High-temperature gel-permeation chromatography (GPC) of these fractions showed (Table 1) that the DMF-insoluble fractions (with the exception of non-substituted PARV **9**) have higher molecular weight. The fractions insoluble in DMF are soluble in *N*-methylcaprolactam at 140 °C, the molecular weight of the polymer being related to its solubility. Among the polymers synthesised, all substituted PARV **10**–**13** are more soluble than non-substituted **9**, the phenyl-substituted polymer **12** being the most soluble one. It is well soluble in chloroform and styrene.

Synthesis of PARV according to Scheme 1 was also performed with the reaction time extended to 48 h and chloroform used as a solvent.[58–60] The reaction employed the 1,4-dibromides **8** with the following substituents R^1 = H, R^2 = H, Me, Ph, CF_3, F, NO_2; R^1 = F, R^2 = CF_3. In all cases, the PARV obtained comprised two fractions, a chloroform-soluble one and an insoluble one; the yield of the former was 0%–55%.

Additionally to the synthesis according to Scheme 1, two other approaches were used in order to obtain PARV with improved solubility.[58–60] The first approach was to use substituted and non-substituted 4,4′-dibromobiphenyls; in the second, at least two haloarenes of different structures were used in the reaction with ethylene.

The former approach is based on the fact that aromatic rings in biphenyl fragments are not coplanar and can rotate with respect to one another.



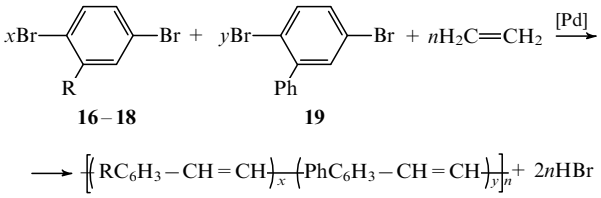


14, **15**

R = H (**14**), Me (**15**).

The introduction of substituents in dibromobiphenyl monomer results in enhanced non-coplanarity of these rings and, hence, lower length of conjugated segments in PARV chain. This change is reflected in the physical properties of the polymer. Thus the PARV **14** based on 4,4′-dibromobiphenyl does not melt and is insoluble in organic solvents; its colour is light-yellow. At the same time, PARV **15** based on 2,2′-dimethyl-4,4′-dibromobiphenyl is colourless, it is low-melting and dissolves well in chloroform and *N*-MP; its molecular weight measured using GPC is 10 700.

Reduced regularity of PARV structure, which is achieved when ethylene reacts with different substituted dibromobenzenes constitutes the basis of the second approach.



16–**18** **19**

R = H (**16**), Me (**17**), NO_2 (**18**).

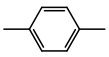
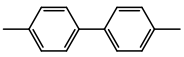
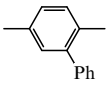
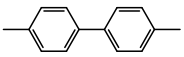
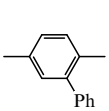
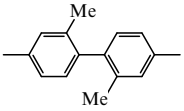
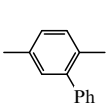
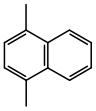
Some properties of random copolymers prepared according to the second method [59] are presented in Table 2. Expectedly, the

Table 2. Some properties of random copolymers based on substituted *p*-dibromobenzenes **16**–**18** and 2,5-dibromobiphenyl **19**.[59]

R	*x*	*y*	Yield,[a] (%)	T_g /°C	Fraction A [b] (%)	M_w [c]	Solubility [d] in *N*-MP at 150 °C
H	0.50	0.50	78	133	33	2030	*ps*
Me	0.50	0.50	93	154	67	4100	*s*
NO_2	0.02	0.98	96	180	70	7490	*is*
	0.05	0.95	92	175	62	15 000	*ps*
	0.10	0.90	100	162	91	7800	*ps*
	0.20	0.80	95	152	78	8600	*ps*
	0.25	0.75	88	156	62	4800	*s*
	0.35	0.65	94	–	78	5400	*s*
	0.40	0.60	97	173	51	6750	*ps*
	0.50	0.50	96	–	48	3120	*ps*

[a] Calculated without account of bromine content. [b] Fraction A is soluble in chloroform; percentage of the total yield of the polymer. [c] M_w for fraction A determined by GPC with polystyrene standard. [d] Hereinafter *s* denotes soluble; *is*, insoluble, and *ps*, partially soluble polymer.

Table 3. Some properties of the random copolymers **20** based on binuclear and condensed dibromoarenes prepared according to Scheme 2.[59]

—Ar—	—Ar′—	*x*	*y*	Yield [a] (%)	Fraction A [b] (%)	M_w [c]	T_g /°C	Solubility in *N*-MP at 150 °C
		0.50	0.50	92	12	500	–	is
		0.50	0.50	87	68	1830	132	ps
		0.25	0.75	83	77	1070	135	ps
		0.50	0.50	50	92	9200	134	s
		0.25	0.75	71	88	6600	145	s
		0.50	0.50	75	88	5330	174	is

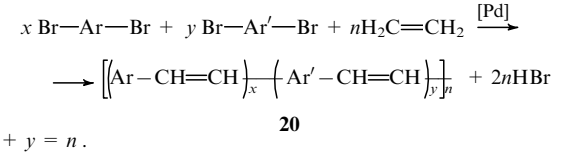
[a] Calculated without account of bromine content. [b] Fraction A is soluble in chloroform; percentage of total yield of the polymer. [c] M_w for fraction A determined by GPC with polystyrene standard.

copolymers with different substituents in phenylene fragments often have a similar or improved solubility compared to corresponding homopolymers.

Analysis of the properties of copolymers based on dibromide **18** (homopolymer is insoluble) and 2,5-dibromobiphenyl **19** (soluble homopolymer) showed that they all are soluble, the solubility being nonlinearly dependent on the content of nitro-substituted phenylene groups (most soluble is the copolymer containing ~25% of such groups).

Copolycondensation of ethylene with binuclear and condensed dibromoarenes yields PARV **20**, which also have lower structural regularity (Scheme 2).

Scheme 2



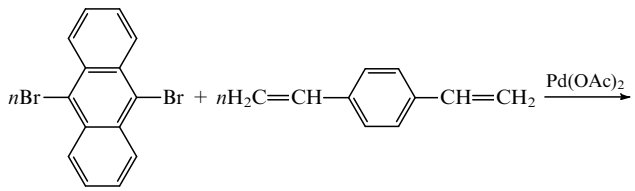
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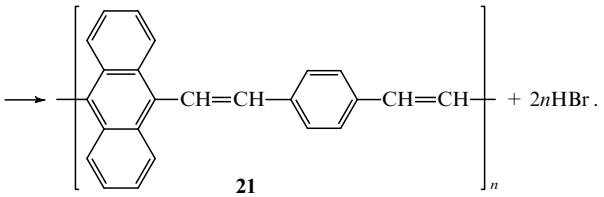
$x + y = n$.

The properties of copolymers **20** presented in Table 3 show that irregularity of the distances between vinylene groups does not noticeably affect solubility of copolymers, whereas introduction of alkyl substituents in initial aromatic compounds enhances solubility.

The synthesis of PARV by reaction of haloarenes with divinylaromatic compounds was considered in Refs 61–67.

An attempt was made [61,67] to obtain anthracene-containing PARV by the Heck's reaction in DMF at 90 °C with a palladium acetate–tris(*o*-tolyl)phosphine–triethylamine catalytic system; the reaction time was 24 h. The reactions of 9,10-divinylanthracene with various dihaloarenes did not produce the desired product, whereas reaction of 9,10-dibromoanthracene with *p*-divinylbenzene gave PARV **21** in nearly quantitative yield.



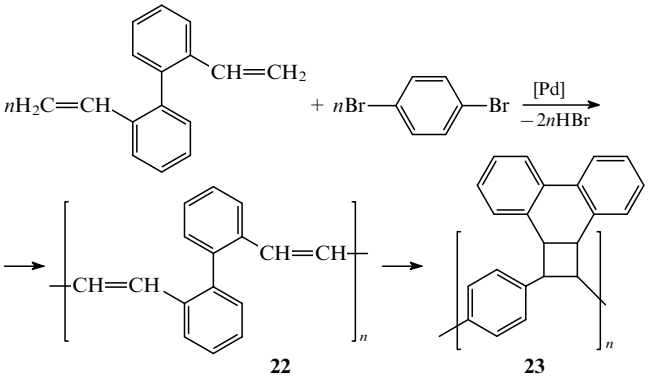


21

The solubility of PARV **21** in organic solvents is very low; therefore it precipitates from the reaction mixture in the course of polycondensation. This results in termination of the chain growth and formation of a low-molecular-weight product. This is confirmed by the data on the molecular weight of the polymer **21** (M_w = 1000) and bromine content (15.4%). In order to enhance solubility of PARV, 2-*tert*-butyl-9,10-dibromoanthracene was used as the initial dibromoanthracene. The oligomer based on it had higher molecular weight; the DMF-soluble fraction had M_w = 1300 and insoluble one, M_w = 1500.

Photosetting PARV **22** were obtained by Müllen *et al.*[63] by the reaction of 2,2′-divinylbiphenyl with *p*-dibromobenzene (Scheme 3). Upon UV-irradiation of the polymer **22** in solution or in solid it is transformed into polymer **23** that incorporates dihydrophenanthrene and cyclobutane fragments.

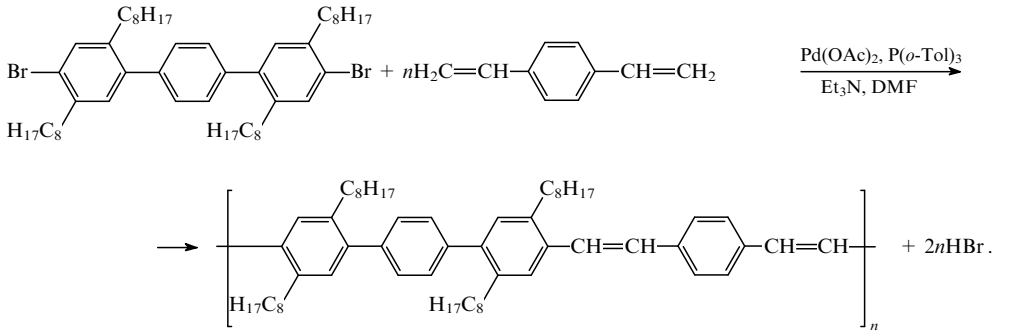
Scheme 3



22 **23**

The PARV **24** that incorporates alternating phenylenebisvinylene and alkyl-substituted terphenylene units was prepared by the reaction of 4,4′-dibromo-2,2″,5,5″-tetraoctyl-*p*-terphenyl with *p*-divinylbenzene (Scheme 4).[64]

Scheme 4

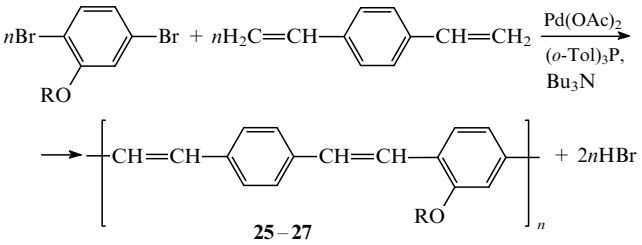


24

According to DSC data, the glass transition temperature of the polymer **24** is −20 °C. The polymer is very soluble in THF, chloroform and toluene; this is due to the presence of long aliphatic substituents, which loosen the polymer structure and reduce intermolecular interactions. Previously long alkyl substituents were introduced in initial monomers in order to produce soluble rigid-chain polymers[68–70] (*viz*. poly-*p*-phenylenes). The GPC measurements of molecular-weight distribution showed that M_w of the polymer **24** is 4500 and polydispersity $M_w/M_n = 1.7$. These data further confirm that the molecular weights depend on their solubility in the reaction mixture; the molecular weight is always higher for the polymers having in their aromatic fragments substituents (*e.g*. aliphatic groups), which enhance their solubility.

Thermogravimetric analysis (TGA) of PARV **24** showed that decomposition of the polymer in N_2 starts at 420 °C. The PARV **24** constituted a basic material for efficient light-emitting diodes (blue light).[59]

Polyarylenes **25**–**27** incorporating side alkoxy groups were obtained in 70%–94% yield by reaction of *p*-divinylbenzene with 2,5-dibromo-1-alkoxybenzenes.[65]



25–**27**

R = n-C_6H_{13} (**25**), n-$C_{12}H_{25}$ (**26**), $CH(C_5H_{11})_2$ (**27**).

It has been shown previously that introduction of alkoxy substituents into initial monomers is an efficient means for reduction of glass transition and melting temperatures and enhancement of solubility of rigid-chain polymers.[71,72] The solubility of alkoxy-substituted PARV depends on the size and structure of a substituent. Thus PARV **25** is insoluble in organic solvents, the polymer **26** has a limited solubility in tetrachloroethane (TCE), and only PARV **27** (M_n = 5400) incorporating 1-pentylhexyl group is well soluble in TCE and chloroform; this is due to reduced (owing to steric hindrance) intermolecular interaction of the polymer chains.[65]

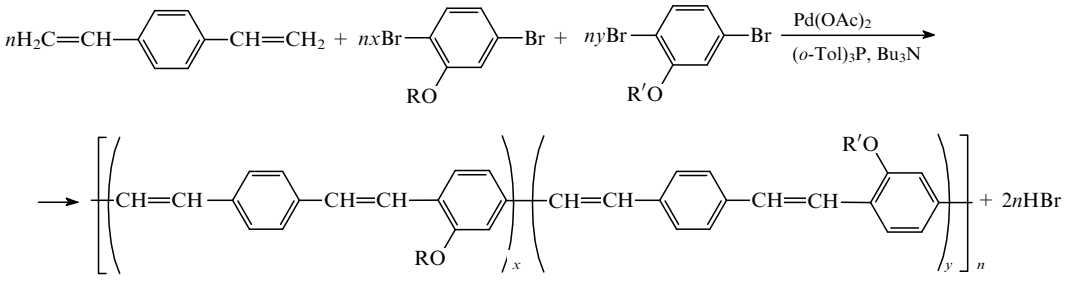
The synthesis of PARV **28**, which incorporate a stilbene chromophore with non-linear optical activity as a substituent (Scheme 5), is also described in Ref. 65. Some properties of the PARV synthesised are presented in Table 4. The polymers containing non-linear optical chromophore and unbranched alkoxy groups are insoluble in organic solvents. Possibly, this is related to the strong intermolecular interaction associated with the presence of large number of polar chromophore groups. Only copolymers containing 50%–70% of $OCH(C_5H_{11})_2$-groups were soluble in TCE or mixtures of TCE with DMF. Similar to the majority of

Table 4. Some properties of PARV **28**.

R	*x*	*y*	Solubility	M_n	Yield (%)	T_g /°C	T_d [a] /°C
without OR-groups	0	1	*is*	–	81	110	399
n-C_6H_{13}	0.5	0.5	*is*	–	88	113	410
	0.1	0.9	*is*	–	68	112	399
n-$C_{12}H_{25}$	0.5	0.5	*is*	–	81	98	396
	0.1	0.9	*is*	–	71	125	360
$CH(C_5H_{11})_2$	0.7	0.3	*s*(TCE)	5000	82	90	370
	0.5	0.5	*s*(TCE, DMF)	5000	73	92	342
	0.1	0.9	*is*	–	89	105	387

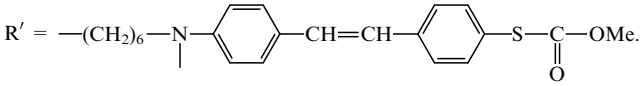
[a] According to DTGA data. Hereinafter T_d is measured in nitrogen atmosphere at the heating rate of 4 deg min^{-1}.

Scheme 5



28

R = n-C_6H_{13}, n-$C_{12}H_{25}$, $CH(C_5H_{11})_2$;

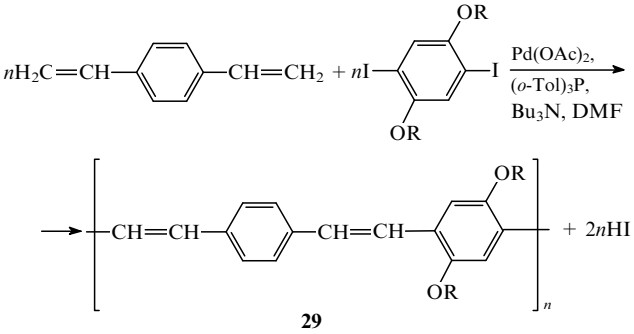
R′ = 

PARV, these copolymers have moderate molecular weights (M_n = 5000).

Studies of the physical properties of these polymers showed that they possess photoinduced conduction and electrooptical activity but do not manifest photorefraction.

Some of the homo- and co-polymers synthesised have liquid-crystal properties and form nematic mesophases. This is related [65] to the rigidity of macromolecular backbones of PARV containing stilbene and distyrylbenzene fragments.[73, 74]

Soluble and meltable PARV **29** with conjugated chains that have mesomorphic properties were obtained [66] by reaction of *p*-divinylbenzene with dialkoxy-substituted *p*-diiodobenzenes.

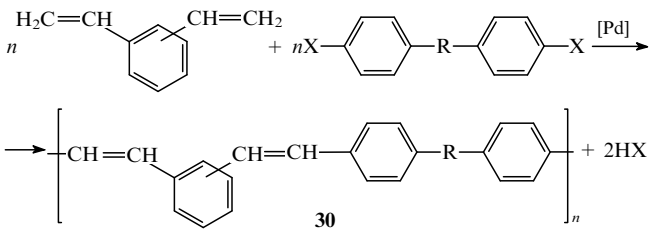


29

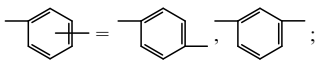
R = C_nH_{2n+1} (n = 4, 7, 8, 12, 16).

All the polymers synthesised are well soluble in THF, chloroform, toluene and dichloroethane. This allowed determination of their molecular weight characteristics (Table 5) and some structural studies. The TGA data show that PARV **29** are stable in nitrogen atmosphere up to 430 °C and DSC shows that their glass transition temperatures (second-order transitions) are in the range of 33–46 °C and decrease with shorter side chains (Table 5). All DSC curves exhibit at least two transitions, which are related to melting of the side and backbone chains (Table 6), the distinct melting temperatures decreasing with longer side chains (nematic mesophases form at the temperatures above melting point).

Thermotropic liquid-crystalline PARV **30** incorporating mesogenic groups and spacers in their backbone chain were synthesised by reactions of *m*- and *p*-divinylbenzenes with diiodo- and dibromo-arylenes containing various bridge groups (DMF or pyridine as solvents, 75–120 °C).[67]



30



; X = Br, I;

R = $(CH_2)_8$, $O(CH_2)_{12}O$, $O(CH_2CH_2O)_4$, $OCO(CH_2)_{10}COO$.

Depending on the nature of the monomers used, the polycondensations were either homogeneous or heterogeneous. Iodoorganic compounds proved to be more reactive than bromoaromatics [the latter required higher concentrations of the catalysts and higher temperatures (to 120 °C)]. The properties of PARV obtained are presented in Table 7.

Table 7. Some properties of PARV **30**.[67]

	–R–	Yield (%)	Content of halide (%)
I–C_6H_4–R–C_6H_4–I			
–(1,3-C_6H_4)–	–O–$(CH_2CH_2O)_4$–	94 [a]	1.08
–(1,4-C_6H_4)–	–O–$(CH_2CH_2O)_4$–	99	2.74
–(1,3-C_6H_4)–	–O–$(CH_2)_{12}$–O–	73	0
–(1,4-C_6H_4)–	–O–$(CH_2)_{12}$–O–	96	8.71
Br–C_6H_4–R–C_6H_4–Br			
–(1,3-C_6H_4)–	–OCO–$(CH_2)_{10}$–COO–	69 [b]	3.31
–(1,4-C_6H_4)–	–OCO–$(CH_2)_{10}$–COO–	81	6.72
–(1,3-C_6H_4)–	–$(CH_2)_8$–	69	3.43
–(1,4-C_6H_4)–	–$(CH_2)_8$–	96	2.56

[a] M_w = 14600, M_w/M_n = 1.48. [b] Logarithmic viscosity in *p*-chlorophenol–chloroform solution is 0.51 dl g^{-1}.

Table 5. Some properties of PARV **29**.[66]

R	M_n	M_w	Polydispersity	T_g /°C
C_4H_9	8300	32 000	3.85	–
C_7H_{15}	18 500	49 300	2.66	46
C_9H_{19}	15 800	46 900	2.97	44
$C_{12}H_{25}$	21 800	62 500	2.87	38
$C_{16}H_{33}$	18 700	53 900	2.88	33

Table 6. DSC data for alkoxy-substituted PARV **29**.[66]

R	T_1 /°C	ΔH_1 /J deg^{-1}	T_2 /°C	ΔH_2 /J deg^{-1}	T_3 /°C	ΔH_3 /J deg^{-1}
C_4H_9	see [a]	see [a]	239.0	106.0	325.0	see [a]
C_7H_{15}	73.8	2.48	see [b]	see [b]	see [a]	see [a]
C_9H_{19}	82.0	2.25	see [b]	see [b]	see [a]	see [a]
$C_{12}H_{25}$	69.1	4.90	152.0	10.24	see [a]	see [a]
$C_{16}H_{33}$	66.4	2.75	103	8.52	133.0	103

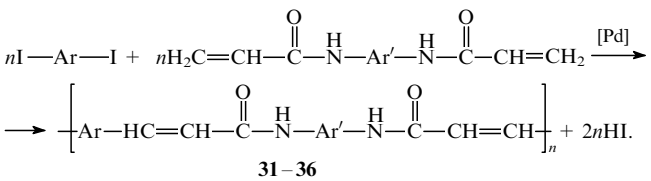
Note. The temperatures and enthalpies of phase transitions are given. Subscript 1 refers to melting of side chains; 2, to the melting of backbone chains, and 3, to nematic/isotropic transition.

[a] Transition was not observed. [b] The temperature and enthalpy of the transition were not determined due to cross-linking of the macromolecules.

The polymers based on *p*-divinylbenzene are insoluble in organic solvents, whereas PARV based on *m*-divinylbenzene and dihaloarenes incorporating ethylene oxide and ester groups are soluble in *p*-chlorophenol and in a mixture of CF_3COOH with $CHCl_3$; the molecular weights of soluble polymers were measured using GPC (they varied within 1400–14 600).

DSC and optical microscopy showed that PARV **30** manifest thermotropic liquid crystallinity. The mesophases of the polymers based on *m*-divinylbenzene and containing ether and ester groups have the smectic texture.

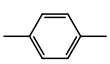
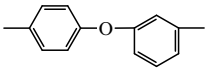
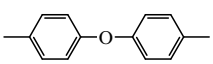
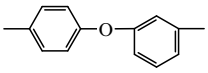
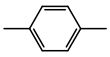
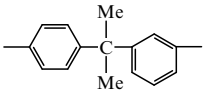
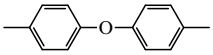
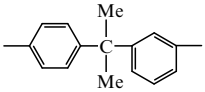
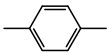
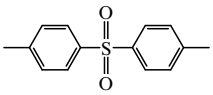
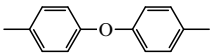
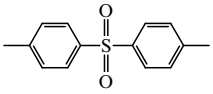
Reactions of unsaturated bisamides with dihaloarenes belong to the same type of processes.[75–85] The synthesis of polycinnamamide **31** from bisacrylamide and aromatic diiodide in the presence of palladium complexes is studied in most detail.



31–36

The polycondensations were performed in various polar aprotic solvents [DMF, dimethylacetamide (DMAA), *N*-MP, DMSO, hexamethylphosphoramide, 1,3-dimethyl-2-imidazoli-

Table 8. Properties of polycinnamamides **31**–**36**.

Compound	–Ar–	–Ar′–	Yield (%)	η_{log} /dl g^{-1}	T_g /°C	T_d (10%) /°C	
						N_2	air
31			99	1.51	–	445	450
32			99	2.60	232	445	445
33			97	1.32	269	395	385
34			94	0.89	238	395	395
35			97	0.26	–	–	–
36			96	0.22	–	–	–

done]; the best results were obtained in DMF. Palladium acetate, palladium chloride and their combinations with triphenylphosphine, tris(*o*-tolyl)phosphine and 1,4-bis(diphenylphosphino)-butane were tested as the catalysts. The polymers with highest viscosity were prepared with a $Pd(OAc)_2$–P(*o*-Tol)$_3$ (1 : 4) catalytic system in the presence of 1,8-bis(dimethylamino)naphthalene as a base. The reaction was performed at 100 °C for 4 h; when the synthesis temperature was increased to 110 °C, the reaction was accompanied by gelation. Polycinnamamides **31**–**34** were prepared in homogeneous conditions. High logarithmic viscosities η_{log} of the solutions indicate that the reaction products are high polymers (Table 8). Thus M_n and M_w of polycinnamamide **32** having viscosity of 2.60 dl g^{-1} are 93 000 and 488 000, respectively. Polycinnamamides **35** and **36** were prepared in heterogeneous conditions and have low logarithmic viscosities.

Polycinnamamides **31**–**36**, with few exceptions, are soluble in pyridine, DMSO, DMAA, *N*-MP and DMF. Strong transparent films were casted from their solutions in DMF.

According to DTG data, the temperatures of decomposition (10% weight loss) for the polycinnamamides are in the range 380–450 °C, the polymers incorporating ether groups being more heat-resistant than those with isopropylidene groups.

The presence of double carbon–carbon bonds in the backbone chains of the polycinnamamides predetermines their capability of curing when heated (>250 °C) or subjected to UV irradiation.

An attempt was undertaken[82] to obtain polycinnamamides under conditions of heterophase catalysis using a palladium–graphite catalyst (Pd–Gr). Such catalysts prepared by metal exchange in potassium-intercalated graphite[84] are known to possess high activity in hydrogenation of alkenes,[85] Heck's reaction[86] and nucleophilic substitution *via* π-allyl complexes.[87]

The synthesis of polycinnamamide **32** was performed in the presence of a Pd–Gr–tributylamine catalytic system in DMF at 100 °C for 20–40 h. Under such conditions, even without a cocatalyst, polymers having logarithmic viscosity of 0.9 dl g^{-1} (which corresponds to the molecular weight of 100 000) can be prepared. Comparison of the results of syntheses of the polycinnamamide on Pd–Gr catalysts and other Pd-containing catalysts is given in Table 9.

Table 9. Comparison of the results of syntheses of polycinnamamide **32** with various palladium catalysts.[82]

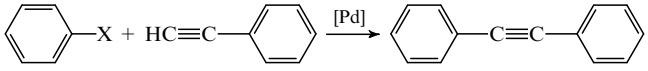
Catalyst	Reaction time /h	Yield (%)	η_{log} /dl g^{-1}
Pd–Gr	4	90	0.25
	20	95	0.90
Pd–Gr–P(Tol-*o*)$_3$	20	96	0.81
Pd–C	20	94	0.69
$Pd(OAc)_2$–P(Tol-*o*)$_3$	4	95	1.11

According to the results obtained, the heterogeneous catalytic reaction proceeds slower than the homophase reaction in the presence of $Pd(OAc)_2$. The reaction on a Pd–Gr catalyst not only has the common advantage of heterophase catalysis (*i.e.*, ease of separation of the catalyst from the reaction products) but also yields polycinnamamides with lower polydispersity and lower palladium content, as compared to similar polymers prepared with $Pd(OAc)_2$.

Generally, the method developed for heterophase synthesis of polycinnamamides[81,82] is simpler than the conventional procedure[88] based on the reaction of biscinnamic acids or their derivatives with diamines.

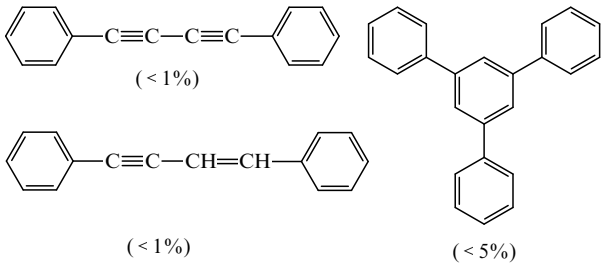
III. Synthesis of polyaryleneethynylenes

The synthesis of PARE is based on the reaction of terminal acetylene groups with a haloaromatic compound.



This reaction is performed in the presence of copper(I) iodide, a base and a palladium salt as a catalyst. Most often $PdCl_2(PPh_3)_2$ is used as catalyst and DMAA and DMF as solvents, although THF[89] and pyridine were also successfully used.

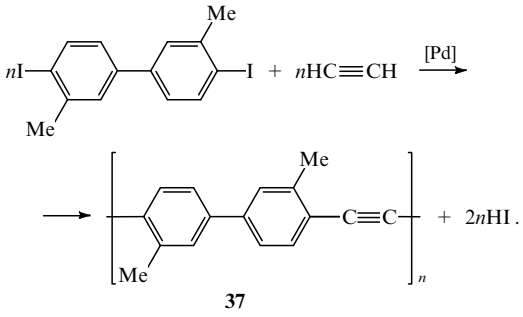
The reaction of iodo(or bromo)benzene with phenylacetylene[39] catalysed by $PdCl_2(PPh_3)_2$ complex also gives by-products,[42] *viz*. diyne, enyne and 1,3,5-triphenylbenzene.



The yields of these compounds, which strongly affect the polycondensation processes, can vary, depending on the reaction conditions;[42] this necessitates the search for the optimal conditions for each particular polycross-coupling.

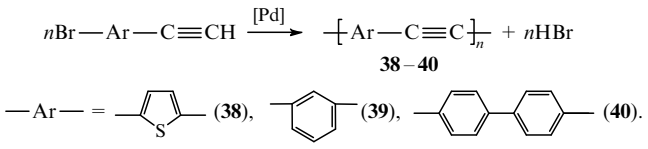
Similar to PARV, polyaryleneethynylenes have been prepared *via* three different ways, namely, by reaction of acetylene with dihaloarenes, by homopolycondensation of haloarylacetylenes and by reaction of diethynylaromatic compounds with dihaloaromatics.

The reactions of acetylene with dihaloarenes, unlike the corresponding reactions with ethylene, did not find wide application. Thus the reaction of 4,4′-diiodo-3,3′-dimethylbiphenyl with acetylene [42] yields the product **37** with low molecular weight due to its insolubility in organic solvents. When heated, the oligomer **37** gives a red anisotropic melt.



37

Homopolycondensation reactions of haloarylacetylenes (AB-type monomers) were studied in detail by Marvel *et al.*[90–92] Homopolycondensations of 2-ethynyl-5-bromothiophene,[90] 3-bromophenylacetylene [92] and 4-bromobiphenylacetylene [91] were performed with the use of a $(Ph_3P)_2PdCl_2-PPh_3-CuI$ catalytic system; the solvent used was triethylamine–pyridine mixture.[32, 36, 39, 93–95]



38–40

The choice of this catalytic system was based on the high yield of the products of cross-coupling.[39, 95] Note, however, that this catalytic system increases contribution of a side reaction, because phenylacetylene polymerises efficiently on this catalyst.[96]

Homopolycondensations were carried out at 90 °C for 2.5–46 h and yielded low-molecular-weight PARE **38–40** (Table 10). The IR spectra of PARE **38–40** did not show the absorption maxima corresponding to terminal ethynyl groups. This is believed [91] to result from oxidative coupling of acetylene groups, occurring in parallel with the major reaction. This side reaction has been described previously.[97, 98]

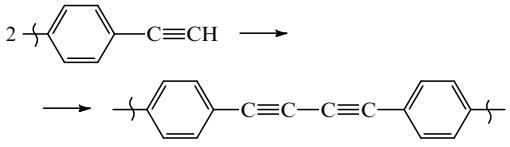


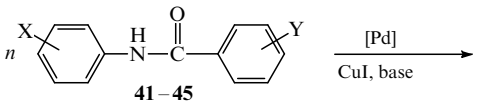
Table 10. Conditions of synthesis and properties of PARE **38–40**.[90–92]

Compound	Composition of solvent (NEt_3 : Py)	Reaction time /h	Conversion (%)	Fraction A [a] (%)	M_w	M_n	Content of Br (%)
38	6 : 4	4.5	23.1	–	2170	1140	13.25
	6 : 4	10	28.6	–	1470	1030	12.12
	6 : 4	15	27.4	–	1440	1020	14.46
39	25 : 17	15	51.2	–	1800	1450	8.86
	17 : 25	15	37.2	–	1650	1270	9.11
	26 : 17	46	40.0	–	2000	1500	8.91
40	15 : 10	2.5	82.6	5.6	2560 [b]	1700 [b]	6.86
	15 : 10	5	89.9	3.1	2480 [b]	1750 [b]	6.18
	15 : 10	10	91.7	3.3	2260 [b]	1630 [b]	7.84
	15 : 10	15	94.2	4.6	2230 [b]	1580 [b]	7.22
	15 : 10	30	95.6	2.8	2780 [b]	2050 [b]	7.11
	12.5 : 12.5	15	92.8	2.9	2440 [b]	1800 [b]	6.79
	3 : 22	15	90.6	6.5	3160 [b]	1940 [b]	6.81

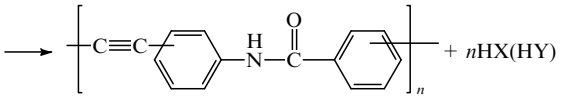
[a] Fraction A is soluble in chloroform. [b] Determined for soluble fractions.

Thermogravimetric studies of PARE **38–40** showed that they are quite stable up to 300 °C, the weight loss in 20 h was less than 10%. The polymers did not melt at 300–400 °C but they gradually darkened and after 20 h of high-temperature ageing turned into black powders.

Synthesis of PARE **46–50** was also based on homopolycondensation of the AB-type monomers **41–45** incorporating amide groups.[99]



41–45



46–50

41, **46**: X = *p*-Br, Y = *p*-C≡CH ; **42**, **47**: X = *m*-Br, Y = *p*-C≡CH ; **43**, **48**: X = *m*-C≡CH, Y = *p*-Br; **44**, **49**: X = *m*-C≡CH, Y = *p*-I; **45**, **50**: X = *m*-C≡CH, Y = *m*-I.

Depending on the nature of the monomers, the reactions proceeded either heterogeneously or homogeneously and the yield of polyaryleneethynyleneamides was 96%–100% (Table 11). When bromine-containing monomers were used, low-molecular-weight products were obtained (η_{log} = 0.12–0.18 dl g^{-1}), whereas polycondensation of the iodine-containing monomer **45** yielded polymer **50** with logarithmic viscosity of

Table 11. Conditions of synthesis and some properties of polyethynyleneamides **46–50**.[99]

Initial monomer	Reaction temperature /°C	Reaction time /h	Yield (%)	η_{log} /dl g^{-1}
41	100	4	100	–
42	100	4	99	0.12
43	100	4	100	0.18
44	100	4	100	–
45	100	4	96	0.43
	80	4	95	0.18
	120	4	100	–
	100	1	96	0.16

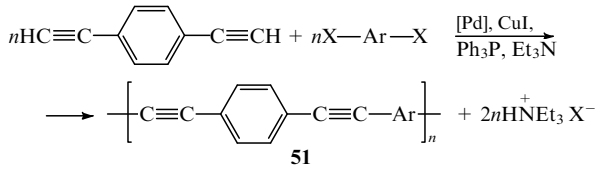
0.43 dl g^{-1}. This result agrees well with the data of Refs 43, 100, which reported higher activity of aryl iodides compared to aryl bromides in palladium-catalysed reactions of oxidative addition.

Studies of solubility of the polymers synthesised showed that simultaneous introduction of amide and *m*-phenylene groups in PARE results in substantially improved solubility of these polymers. Thus high-molecular-weight polymer **50** dissolves in DMF, DMAA, *N*-MP, DMSO, *m*-cresol and pyridine.

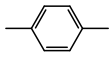
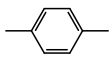
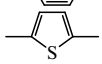
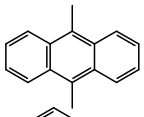
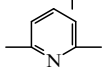
GPC studies of this polymer showed that its M_w is 108 000 and polydispersity M_w/M_n = 16.4, in other words, the polymer has broad molecular-weight distribution. According to TGA data, the temperature of beginning of the decomposition and that of 10% weight loss of PARE **50** are 315 and 350 °C, respectively. DSC showed that an exothermic peak is observed near 270 °C; it is related to the polymer curing *via* the ethynyl groups incorporated in the backbone chains of the macromolecules.

The majority of studies considered synthesis of PARE by reactions of dihaloarenes with diethynylarenes. First works in the field were published in the early 90s.[101, 102] The polyaryleneethynylenes **51** were prepared using two methods.

Method A.

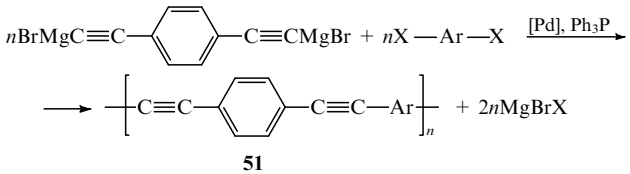


51

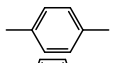
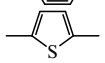
–Ar–	X	Yield of **51** (%)
	Br	79
	I	97
	Br	84
	Br	93
	Br	95

The reactions were carried out for 1–3 h at 80–90 °C in an organic solvent (*e.g.*, toluene) [102] in the presence of CuI and PPh_3. $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ (up to 10 mol.%) were used as catalysts.

Method B.



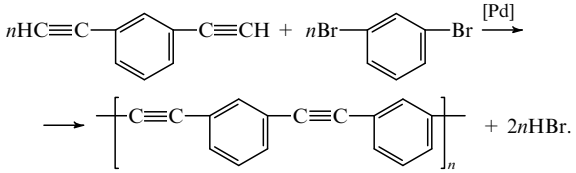
51

–Ar–	X	Yield of **51** (%)
	I	97
	Br	82

The reactions were carried out in THF for 2–3 h at 60–70 °C in the presence of $Pd(OAc)_2$ and PPh_3 or $Pd(PPh_3)_3$.

All the polymers **51** had high crystallinity but were poorly soluble. Therefore their molecular weights could be estimated only on the basis of halide content, which was substantial; most probably the molecular weights were in the range of 1400–4000.

PARE **52** was prepared by the reaction of *m*-dibromobenzene and *m*-diethynylbenzene;[91] this polymer has the structure close to that of the products of homopolycondensation of *m*-bromophenylacetylene (compounds **39**).[94]

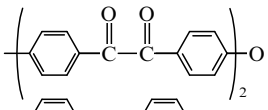
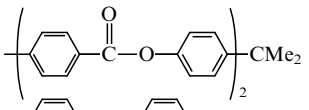
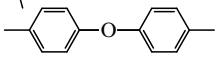
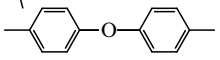
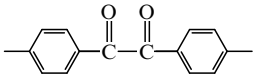
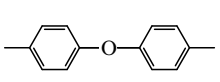
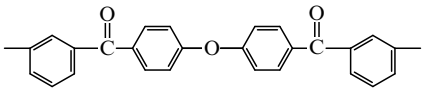
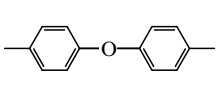
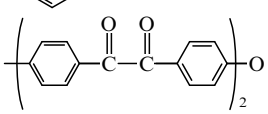
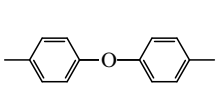


52

The synthesis of polymer **52** was carried out under the same conditions as those for the homopolycondensation of *m*-bromophenylacetylene. The polymer obtained had somewhat higher molecular weight (M_w = 3000). Note that the molecular weight of the polymer determined by means of GPC refers to its soluble fraction (~6%). Generally, this PARE has a very limited solubility. When *p*-dibromobenzene is used as the haloarene, the PARE formed is completely insoluble in organic solvents.

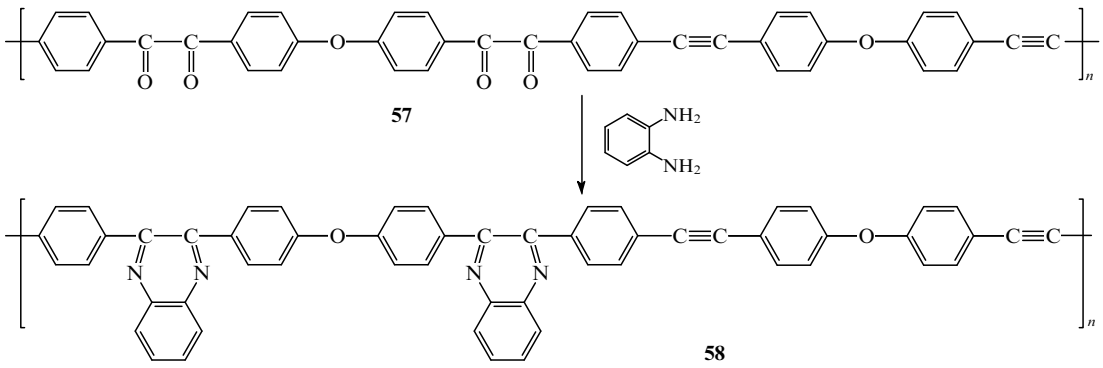
In order to prepare PARE having higher molecular weight and improved solubility, Hergenrother *et al.*[103] used monomers with bridge groups, the 'activated' dibromoaromatic compounds. The solvent used was DMAA. However, virtually all PARE **53**–**57** (Table 12) precipitated from the reaction solutions after

Table 12. Structure and some properties of PARE **53**–**57**.

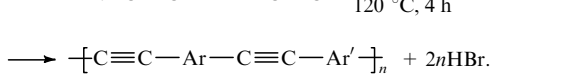
PARE	–Ar–	–Ar′–	η_{log}	T_g [a] /°C	T_{endo} [b] /°C	T_{exo} [c] /°C
53			see [d]	173	–	355
54			see [d]	–	–	343
55			see [d]	–	–	> 350
56			0.28	143	247	320
57			0.27	–	267	333/375

[a] Glass transition temperature determined by DSC at the heating rate of 20 deg min^{-1}; [b] T_{endo} is the melting temperature of crystallites (according to DSC data); [c] T_{exo} is the temperature at which reaction of acetylenic groups starts; [d] PARE are insoluble in TCE, DMAA and *m*-cresol.

Scheme 6



several minutes of stirring at 100–120 °C; this is related to the crystallinity of the polymers.

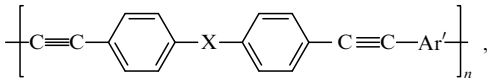


The investigation of PARE **53**–**57** by means of DSC revealed that they manifest endothermic peaks associated with the melting of crystallites and when the polymers are heated they show exothermic effects related to cross-linking *via* the disubstituted acetylenic groups (Table 12).

The polymers based on 4,4′-diethynyldiphenyl ether and dibromides such as 4,4′-bis(4-bromobenzyl)- and 4,4′-bis(3-bromobenzyl)diphenyl ether have limited solubility in TCE in which their viscosity was examined.

The polyaryleneethynylene **57** yields compound **58**, which contains quinoxal-2,3-diyl fragments, upon treatment with *o*-phenylenediamine in TCE (Scheme 6). According to the data of X-ray diffraction,[103] the polymer **58** having T_g = 190 °C, had lower crystallinity than the initial PARE and correspondingly was better soluble in DMAA.

PARE of the type,



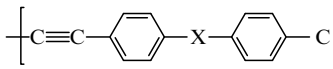
which have the structure and properties close to those of the compounds described in Ref. 103, have been prepared analogously.[104] The polycondensation was carried out in DMAA at 90 °C (in the presence of triethylamine) or at 120 °C (in the presence of tri-n-butylamine) for 4 h with a $PdCl_2(PPh_3)_2$–PPh_3 catalytic system (Table 13).

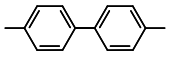
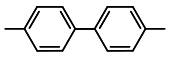
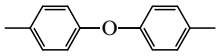
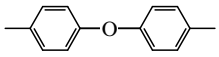
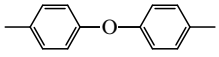
The PARE obtained are insoluble in organic solvents and decompose in H_2SO_4; therefore, their molecular weights were determined from elemental analysis under the assumption that each macromolecule has one terminal bromine atom. The differential thermogravimetry in N_2 shows a small weight loss near 280 °C and less than 5% at 400 °C. The data of DSC indicate that there is a substantial exothermic effect at 250–280 °C; it can be related to thermal cross-linking of the polymer *via* the acetylenic groups.

Similar approach to the preparation of PARE was employed by Rusanov *et al.*[105–107] In order to enhance solubility and to increase molecular weights of the polymers, the monomers containing various bridge groups or aromatic substituents were employed. Thus reaction of 4,4′-diiododiphenyl ether with *p*-diethynylbenzene, 4,4′-diethynyldiphenyl ether and 1,2-bis[4-(4′-ethynylphenoxy)phenyl]-*o*-carborane in DMF at 100 °C during 4 h yielded predominantly products of cross-coupling.[105]

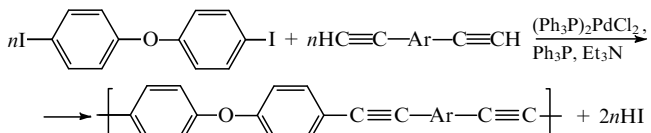
Some properties of the PARE obtained are presented in Table 14. Among the polymers **59**–**61**, the carborane-containing

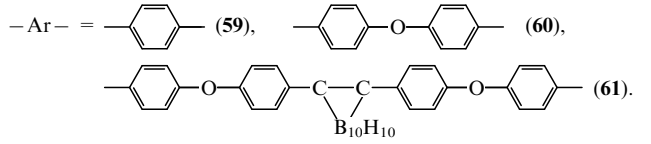
Table 13. Conditions of synthesis [104] and some properties of PARE of type



–X–	–Ar′–	Molecular weight [a]	T_{exo}, /°C	Content of Br (%)
None		500 [b]	–	15.30
–O–		600 [c]	–	13.36
–C(O)–		1000	–	7.83
–O–		550	–	13.83
–C(O)–		1000	260	7.66
None		500	–	15.71
–O–		700	260	11.25
–C(O)–		1100	280	7.00

Note. Solvent is DMAA, temperature is 120 °C.
[a] Calculated on the basis of elemental analysis. [b] Solvent is DMAA, temperature is 90 °C. [c] Solvent is *N*-MP, temperature is 120 °C.





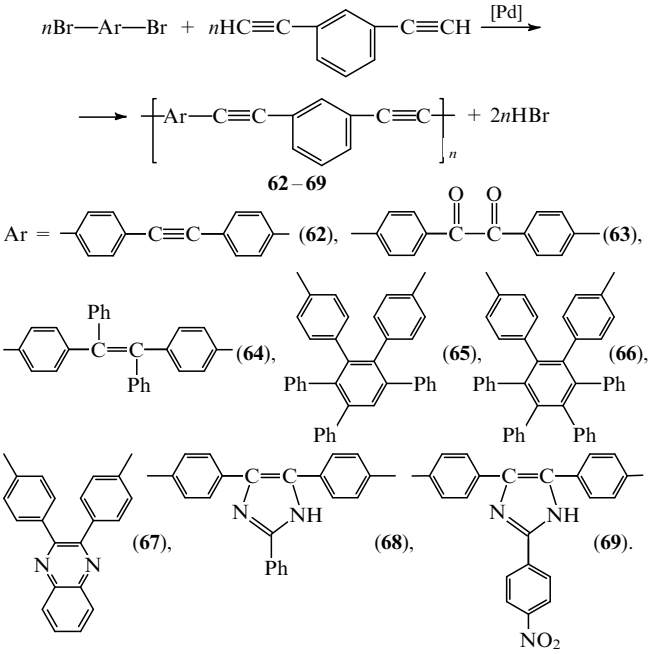
compound **61** is the best soluble one; it is soluble in chloroform and amide solvents. This agrees well with the existing notion [108–110] that carborane groups positively affect solubility of condensation polymers.

Table 14. Some properties of PARE **59**–**61**.[109]

PARE	Yield (%)	Molecular weight [a]	T_g /°C	T_d [b] /°C	Content of I (%)
59	98	820	250	390	15.68
60	82	2400	245	450	5.36
61	80	5500	200	480	0.50

[a] According to the data of ebullioscopy in chloroform or sedimentation in *N*-MP. [b] The temperature of 10% weight loss, DTGA.

A much wider variety of dihaloarenes was used [106, 107] for the synthesis of PARE by reaction of 1,3-diethynylbenzene with various carbo- and hetero-cyclic dibromides.



The reactions were carried out in DMAA at 90 °C for 10 h with the $PdCl_2(PPh_3)_2-PPh_3-CuI-Et_3N$ catalytic system. The data presented in Table 15 show that certain phenyl-substituted PARE are soluble in amide solvents (DMF, DMAA, *N*-MP); this agrees well with the inference [111] that phenyl substituents have a positive effect on the solubility of polyheteroarylenes. Nevertheless, the degree of polymerisation of these PARE calculated on the basis of Br content did not exceed 2–3. It should be noted that the degree of polymerisation of insoluble PARE obtained from dibromides activated by α-diketone, acetylene, ethylene groups and quinoxal-2,3-diyl fragments is also small (3–5). Apparently, solubility of the target compounds in the reaction mixture is a necessary but

Table 15. Properties of PARE **62**–**69**.[109]

PARE	Yield (%)	η_{lim} /dl g^{-1} (DMF)	Content of I (%)	*n* [a]	Solubility
62	72	–	10.65	4	–
63	70	–	12.67	5	–
64	74	–	8.35	4	–
65	72	0.06	16.09	2	DMF, DMAA, *N*-MP
66	74	0.08	11.21	2	–
67	61	–	12.01	3	DMF, DMAA, *N*-MP
68	76	0.09	16.99	3	DMF, DMAA, *N*-MP
69	74	0.07	13.21	3	DMF, DMAA, *N*-MP

[a] Calculated on the basis of elemental analysis.

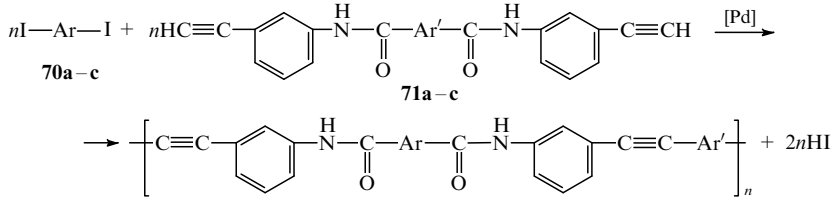
not sufficient condition for synthesis of high-molecular-weight products.

Amide groups were introduced into PARE macromolecules [112] in order to make them soluble in organic solvents; it has been shown previously [99] that in a number of cases this approach gives the desired result. Synthesis of such PARE was performed under usual conditions. In all cases, a small excess of bisethynylarenes was used; this resulted in formation of polymers with improved viscous properties (Scheme 7).

The course of polycondensation depends on the structure of diiodide **70** used. At 1×10^{-3} mol litre^{-1} concentration, polycondensation of *p*-diiodobenzene (**70a**) and 4,4′-diiododiphenyl ether (**70b**) with bisethynylarenes in DMAA proceeded heterogeneously and at half that concentration, homogeneously. Following isolation, majority of the polymers lost their solubility. The polycondensation of 4,4′-diiododiphenyl sulfone (**70c**) always proceeded homogeneously and the polymers obtained were well soluble in DMAA, DMF, *N*-MP, DMSO, *m*-cresol and *o*-chlorophenol.[112] Note that enhanced solubility of diphenyl sulfone-containing polymers, as compared to diphenyl ether-containing, and virtual no effect of diphenylhexafluoroisopropylidene groups on their solubility is quite unusual and falls outside the general structure–solubility dependence in the series of condensation polymers.[113] The properties of the polymers obtained are presented in Table 16. Thus prepared polymers do not show any pronounced glass transition and in TGA experiments in nitrogen atmosphere do not lose weight until 300 °C. At 280 °C, the polymers cross-link *via* acetylenic groups yielding insoluble systems.

The most versatile and reliable method for enhancing solubility of PARE (similar to PARV) is the introduction of long-chain aliphatic substituents into their macromolecules.[114–122] Schulz *et*

Scheme 7



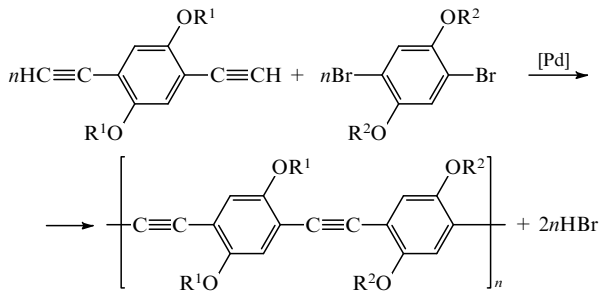
(**a**): Ar = 1,4-C_6H_4, Ar′ = 1,3-C_6H_4;
(**b**): Ar = 4,4′-($C_6H_4-O-C_6H_4$), Ar′ = 5-Bu^t-1,3-C_6H_3;
(**c**): Ar = 4,4′-($C_6H_4-SO_2-C_6H_4$), Ar′ = 4,4′-($C_6H_4-C(CF_3)_2-C_6H_4$).

Table 16. Some properties of PARE based on diiodides **70a–c** and bisethynylarenes **71a–c**.[112]

Bis-ethynyl-arene	Diiodide	Properties of the polymer			
		η_{log} /dl g^{-1} (DMAA, 30 °C)	M_w	M_w/M_n [a]	T_d (10%) [b] /°C
71a	**70a**	–	–	–	365 (450)
	70b	–	–	–	370 (450)
	70c	–	–	–	350 (455)
71b	**70a**	0.72	–	–	355 (465)
	70b	0.43	–	–	
	70c	–	–	–	
71c	**70a**	0.33	17000	1.6	370 (435)
	70b	0.41	26500	1.6	370 (435)
	70c	0.29	12500	1.6	325 (460)

[a] Determined by GPC. [b] The temperatures of the start of decomposition and 10% weight loss as determined by DTGA in air at the heating rate of 10 deg min^{-1}.

al.[114] carried out synthesis of alkoxy-substituted PARE according to the following scheme



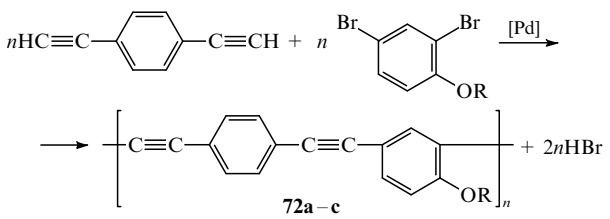
R^1, R^2 = C_4H_9, C_6H_{13}, $C_{11}H_{23}$, $C_{14}H_{29}$, $C_{18}H_{37}$.

1,4-Diethynylbenzene, 9,10-dibromoanthracene and n-alkyl-3,6-dibromocarbazoles were also used for the synthesis of PARE. All the polymers obtained were coloured from yellowish-orange to brown-red and manifested intense fluorescence in aromatic solvents.

The freshly prepared alkoxy-substituted PARE are soluble in boiling toluene, xylene or carbon disulfide. However, after drying *in vacuo* at 30–40 °C only polymers with long side chains (R^1, R^2 = $C_{14}H_{29}$ or $C_{18}H_{37}$) retain solubility. The polymer with R^1 = R^2 = $C_{18}H_{37}$ has the highest solubility (up to 3 g litre^{-1} in hot toluene). The molecular weight of this polymer determined using GPC and osmometry is 8500–10 000; this corresponds to a degree of polymerisation within the range 9–15. This polymer is a meltable product that forms a transparent viscous melt at ~100 °C. At temperatures ⩾170 °C, the polymer cross-links. Films with moderate mechanical properties were prepared from its solution.

DTGA of alkoxy-substituted PARE showed that their decomposition in nitrogen starts at 420 °C. In air decomposition proceeds in two stages, the first stage (70% weight loss) being associated with the cleavage of the side chains and the second, with oxidation of the backbone chains of the polymer.

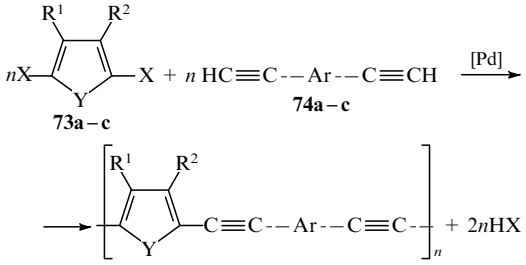
The alkoxy-substituted PARE **72a–c** with *m*-phenylene groups were obtained by reaction of 1,4-diethynylbenzene with 1-alkoxy-2,4-dibromobenzenes.[115]



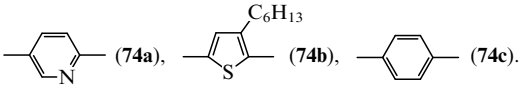
R = $C_{16}H_{33}$ (**a**), $C_{18}H_{37}$ (**b**), $C_{22}H_{45}$ (**c**).

The yields and processibility of the products can be improved through an increase in the length of the substituents. Thus polymer **72c** is soluble in chloroform, benzene, THF, DMF and CS_2; its molecular weight (GPC in DMF) is 40 000; this provides a possibility of casting a good quality film from its chloroform solution.

Synthesis of PARE incorporating heterocycles in their backbone chains was investigated in a number of studies.[116–119]



73a: X = I, Y = S, R^1 = H, R^2 = n-C_6H_{13};
73b: X = Br, Y = Se, R^1 = R^2 = H;
73c: X = Br, Y = S, R^1 = R^2 = NO_2;

Ar =  (**74a**), (**74b**), (**74c**).

The syntheses were carried out in anhydrous toluene according to the method described in Ref. 102 (Table 17). The polyaryleneethynylenes based on diethynylpyridine **74a** and dihalides **73b** and **73c** are soluble only in HCOOH, whereas based on **73a** polymer incorporating hexylthiophene fragments is soluble in $CHCl_3$, CH_2Cl_2, THF, DMF and toluene. This indicates that alkyl substituents positively influence the solubility of PARV and PARE. The choice of 2,5-diethynylpyridine was based on the solubilising effect of pyridine-2,5-diyl groups on rigid-chain polymers.[123, 124]

Table 17. Conditions of synthesis and molecular weights of PARE based on compounds **73** and **74**.

Initial compounds		Conditions of synthesis				Yield (%)	M_w [a]
		$Pd(PPh_3)_4$ (mol.%)	CuI (mol.%)	T /°C	t /h		
73a	**74a**	1	2	110	2.5	100	4.8
	74a	1	2	50	1.5	100	4.3
	74b	5	4	60	5	88	1.9
	74c	1	2	110	2	93	0.96
73b	**74a**	2	5	60	2	100	–
73c	**74a**	2	2	60	19	86	9.6 [b]

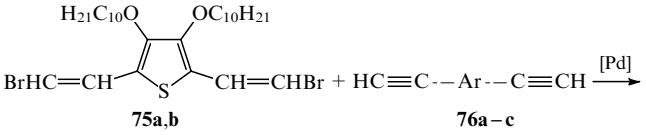
[a] Determined using light scattering in chloroform. [b] Light scattering in HCOOH.

Virtually all the PARE obtained had high molecular weights. Strong films with non-linear third-order optical sensitivity $\chi^{(3)} = 5 \times 10^{-11}$ (cgs) were prepared from their solutions. All the compounds have high degrees of depolarisation ($\rho_v = 0.005 - 0.034$), which, nevertheless, are much lower than $\rho_v = 0.33$ observed for rigid-chain poly(pyridine-2,5-diyl) with the polymerisation degree of 50.[122,123] The polymers manifest fluorescence in solutions; λ_{max} in their spectra are shifted to the long-wave region.

Polyaryleneethynylenes incorporating electron-donor (OAlk) or electron acceptor (OCOAlk) substituents were synthesised[120–122] using the $PdCl_2 - Cu(OAc)_2 - PPh_3$ catalytic system in Et_3N–THF solution. The use of THF, which is capable of solvating metal complexes (it is poor solubility of intermediate complexes that prevents formation of high-molecular-weight PARE[125]) and the presence of alkyl substituents in the monomers provide a possibility to obtain polymers with molecular weights up to 100 000. The optical properties of these polymers are presented in Table 18.[121]

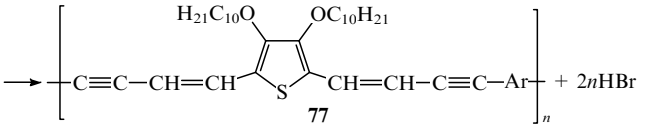
Oligomers (trimers and pentamers), which are better soluble than their high-molecular-weight analogues,[122] form mesophases when heated. These oligomers are used in preparation of oriented materials for optoelectronics. The oligomers with short side chains show the best non-linear optical properties.

Some studies were devoted to the synthesis of PARE based on monomers incorporating vinylene groups.[126,127] Such reactions usually yield polyenynes. Conjugated polyenynes incorporating thiophene fragments were obtained by reaction of 3,4-didecyloxy-2,5-bis(2-bromoethynyl)thiophene with diethynylbenzenes **76a–c** in the presence of $PdCl_2(PPh_3)_2 - CuI$ in Et_3N–THF mixture.[126]

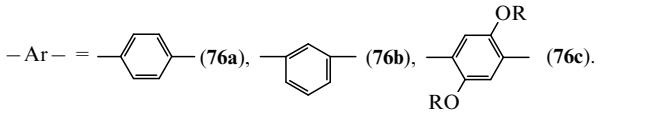


75a,b **76a–c**

75a: *trans*,*trans*; **75b**: *cis*,*trans*



77



The properties of the thus synthesised polyenynes are presented in Table 19. Thin films were casted from solutions of these polymers.

Table 18. Optical properties of alkoxy- and alkoxycarbonyl-substituted oligomers and corresponding polymers.[121]

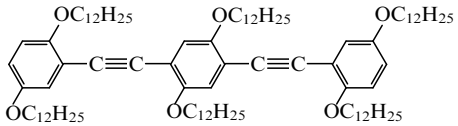
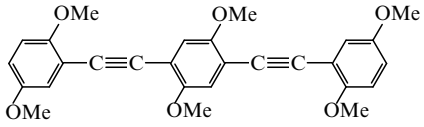
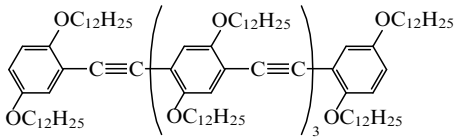
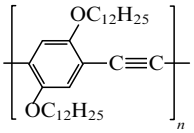
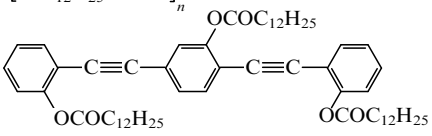
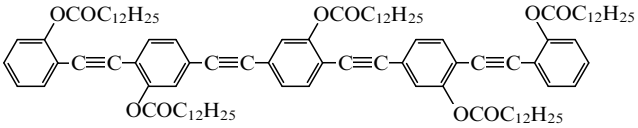
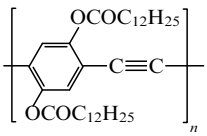
Compound	λ_{max} in luminescence spectra /nm		$\nu_{vis}(C \equiv C)$ in Raman spectra /cm^{-1}	$10^{10}\chi^{(3)}$ (DFWM, 620 nm) /cgs
	solution	film		
	376	378	2207	–
	378	383	–	2.5
	418	425	2200	3.6
	400	419	–	–
	344	337	–	–
	364	375	2204	–
	384	403	–	4.6

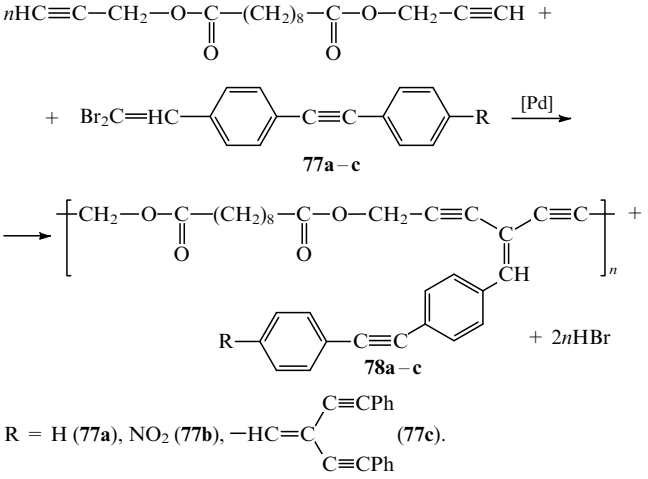
Table 19. Some properties of poly(thiopheneenyne)s **77**.[126]

Initial compounds		$[\eta]$ [a] /dl g^{-1}	T_{exo} /°C	T_d^1 /°C	T_d^2 /°C
75a	**76a**	0.32	300	281	496
	76b	0.27	380	237	532
	76c	0.90	350	325	548
75a + **75b**	**76b**	0.74	350	328	534

[a] Measured in THF at 30 °C.

Upon isolation and drying, the polymers lost solubility in THF. DSC studies showed that all the polymers manifest exothermic effects at 300–380 °C, which correspond to the thermal transformation of acetylene groups. The TGA curves suggest that the decomposition proceeds in two stages, the first stage at 281–328 °C and the second, at 496–548 °C.

The polyenynes **78** with quite unusual structures incorporating isolated conjugated segments were obtained by the reaction of dipropargyl sebacate with 2,2-dibromovinyl-substituted diphenylacetylenes.[127]



The catalytic system used was $PdCl_2[(PTol\text{-}p)_3]_2$–$(PTol\text{-}p)_3$–CuI–$Et_3N$. The synthesis was carried out in boiling dioxane for 24 h. All reactions proceeded homogeneously and yielded polymers soluble in THF, $CHCl_3$ and CH_2Cl_2 with relatively high molecular weight and narrow molecular weight distribution (polydispersity of 1.4–1.6) (Table 20).

Table 20. Some properties of polymers **78a**–**c**.[130]

Polymer	M_w	T_{exo} [a] /°C	T_d (5%) [b] /°C
78a	23000	190	240
78b	18000	183	250
78c	41000	175	340

[a] Data of DSC. [b] Data of DTG.

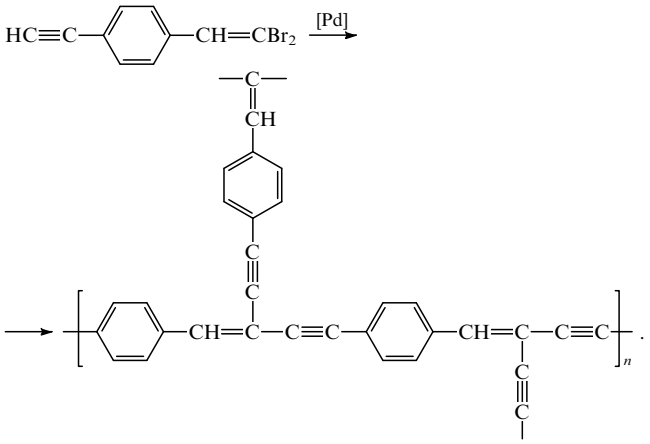
All the polymers have the glass transition temperature of ~60 °C. According to the TGA data, the polymers lose 5% of their weight at 240–340 °C, the polymer **78c** having the highest thermal stability; this is explained by higher content of triple bonds that form a dense cross-linked structure upon heating. The thermal transformations of the acetylene groups are confirmed by the exothermic effect at 175–190 °C (DSC data). All the polymers show non-linear third-order optical sensitivity ($\chi \approx 10^{-10}$ cgs). The polymer **78c** is luminescent (blue light) in solution and solid state.

IV. Conclusion

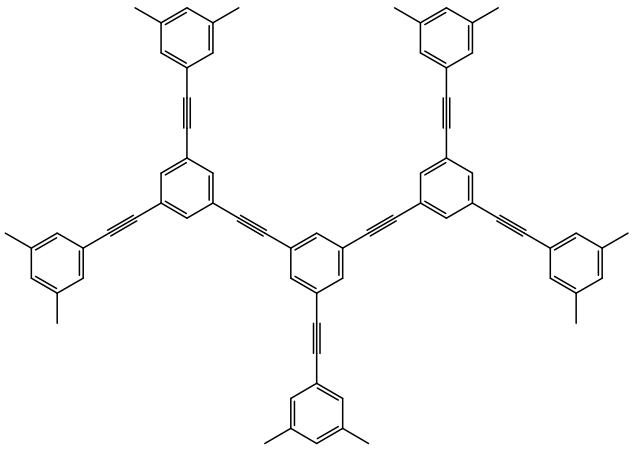
Analysis of the data considered in this review shows that substantial progress in the synthesis of PARV and PARE was achieved in this decade. These compounds have evolved from low-molecular-weight and unprocessible materials to (in some cases) high-molecular polymers soluble in common organic solvents. It is shown that polymers with higher molecular weights can be prepared when long alkyl or, better, alkoxy substituents are introduced as side chains in the monomers. Nevertheless, the search for optimal ways to produce high-molecular soluble polymers in this field remains a topical problem.

The most promising are the studies aimed at development of new types of branched PARV and PARE macromolecules and also improved methods for the synthesis of linear conjugated polymers.

A synthesis of such uncommon macromolecular forms as dendritic (highly branched) polymers has also been reported.[128–131] Thus homopolycondensation of 4-ethynyl-β,β-dibromostyrene yields high-molecular-weight enyne polymer, which is soluble in organic solvents.[128]



Dendritic polymers of arylacetylene family of the general formula



were prepared [129–132] by a reaction of 1,3,5-triethynylbenzene with 1,3,5-tribromobenzene or monomers of 1,3-diethynyl-5-bromobenzene type. Taking into account that the dendrite polymers are usually much better soluble than their linear analogues (when isolated before the gel point),[132–134] one may predict that this approach in chemistry of PARV and PARE will find considerable development.

References

1. T A Skotheim (Ed.) *Handbook of Conducting Polymers* (New York: Marcel Dekker, 1986)
2. W R Salaneck, D L Clark, E J E Samuelsen, in *Science and Application of Conducting Polymers* (New York: Adam Hilger, 1990)
3. J M Andre, J Delhalle, J-L Bredas, in *Quantum Chemistry Aided Design of Organic Polymers* (London: World Scientific, 1991)
4. *Electronic Properties of Conjugated Polymers*. (Eds H Kuzmany, M Mehring, S Roth) (Berlin: Springer, 1989)
5. A J Heeger, D Moses, M Sinclair *Synth. Met*. **17** 143 (1987)
6. M Mehring, D S Cherla, J Zyss (Eds), in *Nonlinear Properties of Organic Materials and Crystals* Vol. 2 (Orlando: Academic Press, 1987) p. 85
7. T Yamamoto *Prog. Polym. Sci*. **17** 1153 (1992)
8. Y Imai, M Yoneyama *J. Synth. Org. Chem. Jpn*. **51** 794 (1993)
9. A-D Schlüter, G Wegner *Acta Polym*. **44** 59 (1993)
10. A L Rusanov, I A Khotina *Usp. Khim*. **65** 852 (1996) [*Russ. Chem. Rev*. **65** 785 (1996)]
11. T A Skotheim (Ed.) *Handbook of Conducting Polymers* (Basel: Marcel Dekker, 1989)
12. J R Reynolds, M Pomerantz, in *Electroresponsive Molecular and Polymeric Systems* Vol. 2 (Ed. T A Skotheim) (Basel: Marcel Dekker, 1991)
13. T Kaino, K I Kubodera, S Tomura, T Kurihara, S Saito, T Tsutsui, S Tokito *Electron. Lett*. **23** 1095 (1987)
14. J H Burroughes, D D Bradley, A R Brown, R N Marks, K Mackay, R H Friend, P L Burns, A B Holmes *Nature* (*London*) **347** 539 (1990)
15. D Braun, A J Heeger *Appl. Phys. Lett*. **58** 1991 (1982)
16. D D C Bradley *Adv. Mater*. **4** 756 (1992)
17. D Clery *Science* **263** 1700 (1994)
18. N C Greenham, S C Moratti, D D C Bradley, R H Freund, A B Holmes *Nature* (*London*) **365** 628 (1993)
19. W Tachelet, S Jacobs, H Ndayikengurukiye, H J Geise *Appl. Phys. Lett*. **64** 2364 (1994)
20. Z Yang, I Sokolic, F E Karasz *Macromolecules* **26** 1188 (1993)
21. R N McDonald, T N Campbell *J. Am. Chem. Soc*. **82** 4669 (1960)
22. L Rajaraman, M Balasubramanian, M Nanjan *J. Curr. Sci*. **49** 101 (1980)
23. W J Feast, I S Millichamp *Polym. Commun*. **24** 102 (1983)
24. D R Gagnon, J D Capistran, F E Karasz, R W Lenz *Polym. Bull*. **12** 293 (1984)
25. S Antoun, F E Karasz, R W Lenz *J. Polym. Sci., Part A, Polym. Chem*. **26** 1089 (1988)
26. V P Conticello, D L Gin, R G Grubbs *J. Am. Chem. Soc*. **114** 9708 (1992)
27. I Murase, T Ohnishi, T Noguchi, M Hirooka *Polym. Commun*. **25** 293 (1984)
28. S Tokito, T Tsutsui, S Saito *Polym. Commun*. **27** 333 (1986)
29. H-H Hörhold, H J Calme, R Bergmann *Faserforsch. Textiltechn*. **29** 299 (1978)
30. H-H Hörhold, H Helbig *Makromol. Chem., Makromol. Symp*. **12** 229 (1987)
31. R F Heck, J P Nolly, Jr *J. Org. Chem*. **37** 2320 (1972)
32. H A Dieck, R F Heck *J. Organomet. Chem*. **93** 259 (1975)
33. R F Heck *Acc. Chem. Res*. **12** 146 (1979)
34. R F Heck *Pure Appl. Chem*. **53** 2323 (1981)
35. R F Heck *Org. React*. **27** 345 (1982)
36. R F Heck, in *Palladium Reagents in Organic Synthesis* (New York: Academic Press, 1985) p. 179
37. R F Heck, in *Best Synthetic Methods* (Eds A R Katritzky, G Meth-Cohn, C W Rees) (London: Academic Press, 1985)
38. R F Heck, in *Palladium Reagents in Organic Synthesis* (New York: Academic Press, 1990)
39. K Sonogashira, Y Tohda, N Hagihara *Tetrahedron Lett*. **50** 446 (1975)
40. K Sonogashira, in *Comprehensive Organic Synthesis* Vol. 3 (Eds B M Trost, I Fleming) (London: Pergamon Press, 1990) p. 521
41. K Sonogashira, S Takahashi *J. Synth. Org. Chem. Jpn*. **51** 1053 (1993)
42. W Heitz *ACS Polym. Prepr*. **32** (1) 327 (1991)
43. V Percec, C Pugh, E Cramer, S Okita, R Weiss *Makromol. Chem., Makromol. Symp*. **54**/**55** 113 (1992)
44. K Tamao, K Sumitani, M Kumada *J. Am. Chem. Soc*. **94** 4374 (1972)
45. R J P Corriv, J P Masse *J. Chem. Soc., Chem. Commun*. 144 (1972)
46. K Tamao, K Sumitani, Y Kiso, M Zembayashi, A Fujioka, S Komada, I Nakajiama, A Minato, M Kumada *Bull. Chem. Soc. Jpn*. **49** 1958 (1976)
47. N A Bumagin, N P Andryukhova, I P Beletskaya *Dokl. Akad. Nauk SSSR* **297** 1126 (1987) [a]
48. M Ueda, F Ichikawa *Macromolecules* **23** 926 (1990)
49. M Bochmann, K Kelly *J. Chem. Soc., Chem. Commun*. 532 (1989)
50. M Bochmann, K Kelly, J Lu *J. Polym. Sci., Part A, Polym. Chem*. **30** 2511 (1992)
51. T Horn, U Scherf, S Wegner, K Müllen *ACS Polym. Prepr*. **33** (1) 190 (1992)
52. N Migaura, T Ishiyama, M Ishikawa, A Susuki *Tetrahedron Lett*. **27** 6369 (1986)
53. N Migaura, T Ishiyama, H Sasaki, M Ishikawa, M Satoh, A Susuki *J. Am. Chem. Soc*. **111** 314 (1989)
54. M Brenda, A Greiner, W Heitz *Makromol. Chem*. **191** 1083 (1990)
55. Jpn. Appl. 57-207 618; *Chem. Abstr*. **99** 23 139k (1983)
56. W Heitz, W Brügging, L Freund, M Gailberger, A Greiner, H Jung, U Kampschulte, N Niebner, F Osan, H-W Schmidt, W Wicker *Makromol. Chem*. **189** 119 (1988)
57. A Greiner, W Heitz *Makromol. Chem. Rap. Commun*. **9** 581 (1988)
58. A Greiner, W Heitz *ACS Polym. Prepr*. **32** (1) 333 (1991)
59. H Martelok, A Greiner, W Heitz *Makromol. Chem*. **192** 967 (1991)
60. A Greiner, H Martelok, A Noll, N Siegfried, W Heitz *Polymer* **32** 1857 (1991)
61. H-P Weitzel, K Müllen *Makromol. Chem*. **191** 2815 (1990)
62. H-P Weitzel, K Müllen *Makromol. Chem*. **191** 2837 (1990)
63. K Müllen, A Böhm, G Fiesser, R O Garay, H Mauermann, S Stein *ACS Polym. Prepr*. **34** (1) 195 (1993)
64. A Hilber, H-J Brouwer, B-J van der Scheer, J Wildeman, G Hadziioannou *Macromolecules* **28** 4525 (1995)
65. W-K Chan, L Yu *Macromolecules* **28** 6410 (1995)
66. Z Bao, Y Chen, R Cai, L Yu *Macromolecules* **26** 5281 (1993)
67. M Suzuki, J-C Lim, T Saegusa *Macromolecules* **23** 1574 (1990)
68. W Heitz *Chem. Ztg*. **110** 385 (1986)
69. H Ringsdorf, P Tschirmer, O Hermann-Schünherr, J H Wendorf *Makromol. Chem*. **188** 1431 (1987)
70. M Ballauff *Angew. Chem., Int. Ed. Engl*. **28** 253 (1989)
71. M Ballauff, G F Schmidt *Makromol. Chem. Rap. Commun*. **8** 93 (1987)
72. M Wenzel, M Ballauff, G Wegner *Makromol. Chem*. **188** 2865 (1987)
73. T W Campbell, D N McDonald *J. Org. Chem*. **24** 1246 (1959)
74. W Memeger *Macromolecules* **22** 1577 (1989)
75. US P. 4 937 313; *Chem. Abstr*. **112** 236 385m (1991)
76. M Kakimoto, M Yoneyama, Y Imai, in *Book of Abstracts of the 33th IUPAC International Macromolecular Symposium, Montreal, 1990* p. 227
77. Y Imai, in *Book of Abstracts of the 197th ACS National Meeting, Dallas, 1989* p. 901
78. Y Imai *ACS Polym. Prepr*. **32** (1) 331 (1991)
79. Y Imai *Chemtech* 560 (1991)
80. Y Imai *Makromol. Chem., Makromol. Symp*. **54**/**55** 151 (1992)
81. M Yoneyama, M Kakimoto, Y Imai *Macromolecules* **22** 4148 (1989)
82. M Jikei, Y Ishida, Y Seo, M Kakimoto, Y Imai *Macromolecules* **28** 7924 (1995)
83. M Suzuki, J-C Lim, K Sho, T Saegusa *Polym. Bull*. **21** 415 (1989)
84. D Savoia, C Trombini, A Umani-Ronchi *Pure Appl. Chem*. **57** 1887 (1985)
85. D Savoia, C Trombini, A Umani-Ronchi *J. Chem. Soc., Chem. Commun*. 540 (1981)
86. D Savoia, C Trombini, A Umani-Ronchi, G Verardo *J. Chem. Soc., Chem. Commun*. 541 (1981)
87. G P Boldrini, D Savoia, E Tagliavini, C Trombini, A Umani-Ronchi *J. Organomet. Chem*. **268** 97 (1984)
88. V V Korshak, T M Frunze, in *Sinteticheskie Geterotsepnye Poliamidy* (Synthetic Heterochain Polyamides) (Moscow: Nauka, 1962)
89. M E Wright *Macromolecules* **22** 3256 (1989)

90. D L Trumbo, C S Marvel *J. Polym. Sci., Part A, Polym. Chem.* **24** 2231 (1986)
91. D L Trumbo, C S Marvel *J. Polym. Sci., Part A, Polym. Chem.* **24** 2211 (1986)
92. D L Trumbo, C S Marvel *J. Polym. Sci., Part A, Polym. Chem.* **25** 839 (1987)
93. K Ishizu, U D G Prabbu, D Draney, B H Lee, C S Marvel *J. Polym. Sci., Polym. Chem. Ed.* **20** 2851 (1982)
94. D L Trumbo, C S Marvel *J. Polym. Sci., Polym. Symp.* 74 (1986)
95. L Cassar *J. Organomet. Chem.* **93** 253 (1975)
96. C I Simionescu, V Percec, S Dumitrescu *J. Polym. Sci., Polym. Chem. Ed.* **15** 2497 (1977)
97. A S Hay *J. Org. Chem.* **25** 1275 (1960)
98. V V Korshak, S L Sosin, A M Sladkov *J. Polym. Sci., Part. C, Polym. Symp.* **4** 1315 (1964)
99. S Watanabe, M Tanabe, M Kakimoto, Y Imai *J. Polym. Sci., Part A, Polym. Chem.* **32** 987 (1994)
100. R F Heck *Adv. Catal.* **28** 323 (1977)
101. K Sanechika, T Yamamoto, A Yamamoto *Polym. Prepr. Jpn.* **30** 160 (1981)
102. K Sanechika, T Yamamoto, A Yamamoto *Bull. Chem. Soc. Jpn.* **57** 752 (1984)
103. S J Havens, P M Hergenrother *J. Polym. Sci., Polym. Chem. Ed.* **23** 587 (1985)
104. M Bochman, K Kelly *J. Polym. Sci., Part A, Polym. Chem.* **30** 2503 (1992)
105. I A Khotina, M M Teplyakov, A L Rusanov *Izv. Akad. Nauk, Ser. Khim.* 447 (1994) [b]
106. M L Keshtov, M M Begretov, I A Khotina, A L Rusanov, A K Mikitaev *Izv. Akad. Nauk, Ser. Khim.* 1229 (1996) [b]
107. I A Khotina, M L Keshtov, M M Bergetov, A K Mikitaev, A L Rusanov, in *Proceeding of the 4th European Technical Symposium on Polyimides and High Performance Polymers, 1996* p. I 1
108. N I Bekasova *Usp. Khim.* **53** 107 (1984) [*Russ. Chem. Rev.* **53** 61 (1984)]
109. S V Vinogradova, P M Valetskii, Yu A Kabachii *Usp. Khim.* **64** 390 (1995) [*Russ. Chem. Rev.* **64** 365 (1995)]
110. S V Vinogradova, P M Valetskiy, N I Bekasova *Chem. Rev.* **18** 1 (1993)
111. V V Korshak, A L Rusanov *Usp. Khim.* **52** 812 (1983) [*Russ. Chem. Rev.* **52** 459 (1983)]
112. S Watanabe, M Tanabe, M Jikei, M Kakimoto, Y Imai *J. Polym. Sci., Part A, Polym. Chem.* **33** 2385 (1991)
113. F W Harris, R B Seymour (Eds) *Structure–Solubility Relationships in Polymers* (New York: Academic Press, 1977)
114. R Guesa, R C Schulz *Makromol. Chem.* **191** 857 (1990)
115. K Kondo, M Okuda, T Fujitani *Macromolecules* **26** 7382 (1993)
116. M Takagi, K Kizu, Y Miyazaki, T Maruyama, T Kubata, T Yamamoto *Chem. Lett.* 913 (1993)
117. T Yamamoto, M Takagi, K Kizu, T Maruyama, T Kubata, H Kambara, T Kurihara, T Kaino *J. Chem. Soc., Chem. Commun.* 797 (1993)
118. T Yamamoto *Chem. Lett.* 1959 (1993)
119. T Yamamoto, W Yamada, M Takagi, K Kizu, T Maruyama, N Ooba, S Tomaru, T Kurihara, T Kaino, T Kubata *Macromolecules* **27** 6620 (1994)
120. J LeMoigne, M Moroni, H Coles, A Thierry, F Kajzar *Mater. Res. Soc. Symp. Proc.* **247** 65 (1992)
121. M Moroni, J LeMoigne, S Luzzati *Macromolecules* **27** 562 (1994)
122. P Wautelet, M Moroni, L Oswald, J LeMoigne, A Pham, J-Y Bigot, S Luzzati *Macromolecules* **29** 446 (1996)
123. T Yamamoto, T Ito, K Kubota *Chem. Lett.* 153 (1988)
124. T Yamamoto, T Ito, K Sanechka, M Hishinuma *Chem. Ind.* 337 (1988)
125. I M Brown, J M Wilbur *Macromolecules* **21** 1064 (1988)
126. J J Kane, F Gao, B A Reinhardt, R C Evers *ACS Polym. Prepr.* **32** (1) 1064 (1992)
127. S Fomine, L Fomina, H G Florentino, J M Mendez, T Ogawa *Polym. J.* **27** 1085 (1995)
128. L Fomina, R Salcedo *Polymer* (1997) (in the press)
129. J S Moore, Z Xu *Macromolecules* **24** 5813 (1991)
130. Z Xu, M Kahr, K L Wilkins, J S Moore *J. Am. Chem. Soc.* **116** 4537 (1994)
131. Z Xu, J S Moore *Acta Polym.* **45** 83 (1994)
132. D A Tomalia, A M Naylor, W A Goddard *Angew. Chem., Int. Ed. Engl.* **29** 138 (1990)
133. J Issberner, R Moors, F Vögtle *Angew. Chem.* **106** 2507 (1994)
134. B I Voit *Acta Polym.* **46** 87 (1995)

[a] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[b] — *Russ. Chem. Bull. (Engl. Transl.)*