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Rigid-rod poly(benzobisazoles) and molecular composites based on them

L G Komarova, A L Rusanov

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Abstract. The results of studies in the field of rigid-rod poly(benzobisazoles) and molecular composites based on them are analysed and generalised. Poly(benzobisazoles) are most promising candidates for high-strength and high-modulus polymeric materials, while the molecular composites based on them can be employed in the synthesis of polymeric materials with a broad spectrum of mechanical properties. The bibliography includes 101 references.

I. Introduction

Rigid-rod polymers began to attract the keen attention of investigators after two main hypotheses had been put forward,[1] namely:

1. Those materials which possess high rigidity manifest the highest deformation strengths. In terms of their moduli of elasticity (E) the polymers, all the macromolecules in which are straightened in the same direction, can be equivalent to steel.

2. The polymers with relatively low densities possess high mechanical characteristics. This suggests that the values of specific moduli of rupture and deformation strengths of the straightened macromolecules can be very high.[2]

These statements have predetermined the increased interest of synthetic chemists in the construction of macromolecules which display maximum thermodynamic rigidities.[3]

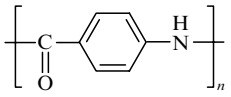
High deformation strengths and rigidities of polymers are provided by covalent bonds between the macromolecules which should manifest high levels of straightness and contain predominantly aromatic rings. These properties also determine the thermal stabilities of the polymers.[3,4]

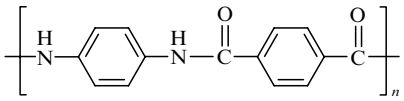
High levels of molecular straightness are more effectively achieved in fibres than in bulk products; therefore, special attention to the design of high-strength fibres for composite materials was given.[3–5]

The first steps in these investigations were aimed predominantly at the preparation of fibres based on aromatic polyamides devoid of non-symmetrical fragments and 'hinge' groups, *e.g.*, poly(*p*-benzamide) and poly(*p*-phenyleneterephthalamide).[6–12]

L G Komarova, A L Rusanov A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 93 27. E-mail: komarova@ineos.ac.ru (L G Komarova). Tel. (7-095) 135 63 72. E-mail: alrus@ineos.ac.ru (A L Rusanov)

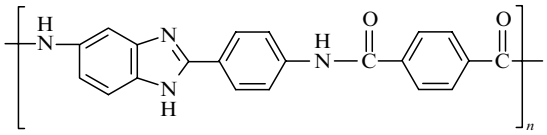
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The latter polymer, which is commonly known under the commercial name Kevlar, and its different modifications are used as the basis for the preparation of high-modulus and high-strength polymeric materials.

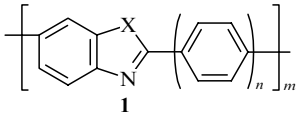
In addition to aromatic polyamides synthesised from carbocyclic diamines and dicarboxylic acids, polyamides based on heterocyclic monomers, *e.g.*, poly[(2-phenylbenzoimidazole-5,4′-diyl)terephthalamide], are of considerable interest.[10]



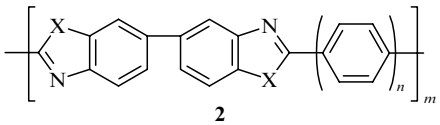
It should be noted however that the presence of amide groups in the macromolecules of these polymers limits their thermal and thermohydrolytic stabilities. Hence, in the second step of investigations in this field, the main attention was focused on rigid-rod polymers which contain only aromatic carbo- and heterocycles,[13–18] the so-called rigid-rod poly(heteroarylenes).

II. Rigid-rod poly(benzazoles)

In the series of rigid-rod polyheteroarylenes, the poly(benzoazoles) (PBAz) **1** and **2** and, particularly, poly(benzobisazoles) (PBBAz) **3a**–**c** or isomeric structures have been studied in especially great detail.[17–23]

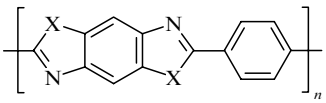


1



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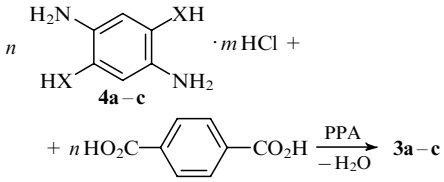
X = NH, NPh, O; n = 1, 2.



3a–c

X = NH (**a**), O (**b**), S (**c**).

High-temperature polycyclocondensation of 1,2,4,5-tetraaminobenzene-,[26] 4,6-diaminodihydroxybenzene-[27] and 2,5-diaminobenzene-1,4-dithiol hydrochlorides[28,29] with terephthalic acid in polyphosphoric acid (PPA)[23–25] is the most popular procedure for the synthesis of the polymers **3a–c**.



4a–c

m = 4, X = NH (**a**); *m* = 2: X = O (**b**), S (**c**).

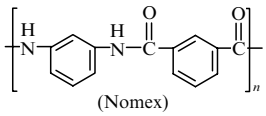
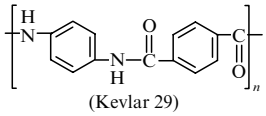
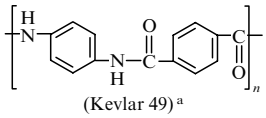
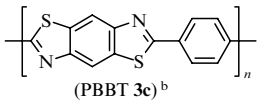
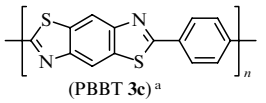
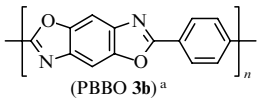
If the synthesis is performed at polymer concentrations which are high enough for the formation of anisotropic solutions, the resulting polymeric solutions can be used directly for the preparation of high-modulus fibres[29,30] and films.[31]

Because of high oxidisability of the tetrafunctional nucleophilic monomers **4a–c**, these are used in the form of hydrochlorides or other salts rather than as free bases. The process is performed in two steps. In the first step which is carried out at 60–80 °C, the nucleophilic monomers are subjected to dehydrochlorination; in the second step, terephthalic acid is added, the mixture is slowly heated to 190–200 °C and stirred at this temperature for 8–10 h.

In the course of polycyclocondensation, the content of P_2O_5 in PPA decreases, and its properties as the solvent, catalyst and cyclodehydrating agent deteriorate. The addition of P_2O_5 to the solutions results in both acceleration of the polycyclodehydration reaction and an increase in the molecular mass of the target polymers.[32–35] In addition to dicarboxylic acids, the respective acid chlorides are also used for the synthesis of PBBAz in a PPA medium.[36] Since the glass transition temperatures of PBBAz often exceed their decomposition temperatures,[14] the fibres and films are usually prepared directly from the solutions of these polymers.

Poly(benzobisazoles) are soluble in strong acids, *e.g.*, PPA, methanesulfonic acid, chlorosulfonic acid, 100% H_2SO_4 and Lewis acids (*e.g.*, $BiCl_3$ or $SbCl_3$). Recently,[37] it was shown that poly(benzobisthiazole) (PBBT **3c**) forms liquid-crystalline solutions in nitromethane containing $AlCl_3$ or $GaCl_3$. Liquid-crystalline solutions of PBBAz yield high-strength and high-modulus films and fibres. Very often, the deformation strength characteristics of PBBAz fibres even surpass those of Kevlar polyamide fibres which is attributed, in particular, to the greater values of the Kuhn segments in PBBAz (see Table 1 and Fig. 1).[38–45]

Table 1. The ultimate rupture strength (σ), the modulus of elasticity (E), the elongation at rupture (ε) and values of the Kuhn segment (A) of fibres based on rigid-rod polymers.

Polymer	σ/GPa	E/GPa	ε(%)	A/Å	Ref.
 (Nomex)	0.70	17.3	22	47	9
 (Kevlar 29)	2.64	58.9	4	300	38
 (Kevlar 49)[a]	2.64	127.5	2.4	300	39
 (PBBT **3c**)[b]	0.5–2.2	50–76	4.5	1060	40, 41
 (PBBT **3c**)[a]	0.8–2.5 (4.2)	76–265 (< 300)	1.0–1.5	1060	42
 (PBBO **3b**)[a]	2.8–3.4	467		–	34, 44

[a] Heat-treated; [b] freshly formed.

The films with controlled planar orientation based on PBBT and PBBO have specific strengths of 2 GPa and moduli of elasticity of 270 GPa.

Poly(benzobisazoles) are distinguished by extremely high thermal stabilities, *viz.*, under conditions of a dynamic thermogravimetric analysis in air (ΔT = 10 deg min^{-1}), they begin to lose weight at temperatures above 600 °C (Fig. 2).[18] Under conditions of an isothermal analysis in circulating air at 371 °C, their thermal characteristics markedly exceed those of poly(*p*-benzamide), PBBT **3c** being much more resistant to heating than PBBO **3b** (Fig. 3).[46]

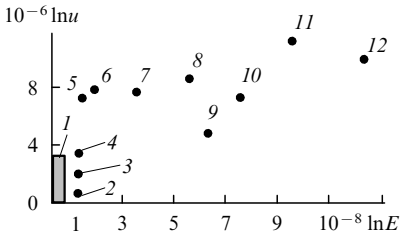


Figure 1. The specific moduli of elasticity (E) and the specific strains (u) of some materials;[45]
(*1*) organic compounds, (*2*) aluminium, (*3*) steel, (*4*) 'E'-glass, (*5*) 'S'-glass, (*6*) Kevlar 29, (*7*) Kevlar 49, (*8*) freshly formed poly(benzobisoxazole) (PBBO **3b**) fibre, (*9*) boron fibre, (*10*) freshly formed poly(benzobisthiazole) (PBBT **3c**) fibre, (*11*) heat-treated PBBT **3c** fibre, (*12*) heat-treated PBBO **3b** fibre.

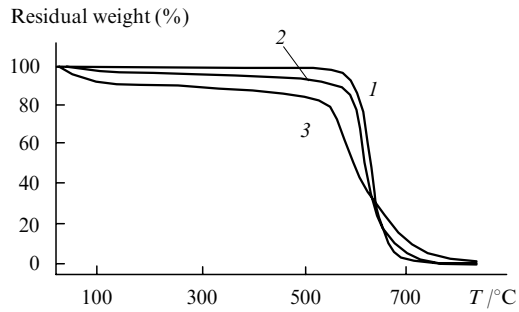


Figure 2. Thermogravimetric analysis of PBBAz in air (the rate of heating is 10 deg min^{-1});[18] (*1*) PBBT, (*2*) PBBO, (*3*) poly(benzobisimidazole) (PBBI **3a**).

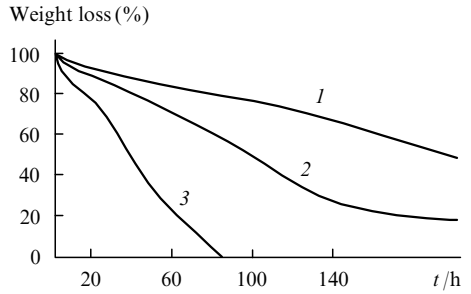
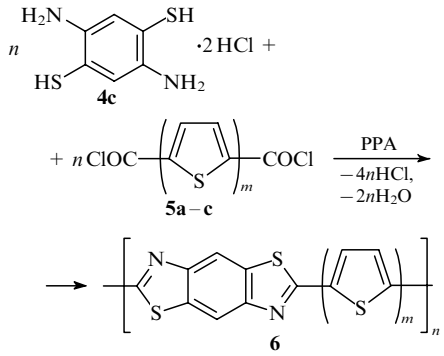


Figure 3. Isothermal ageing in circulating air at 371 °C; (*1*) PBBT **3c**, (*2*) PBBO **3b**, (*3*) poly(benzamide).

A significant disadvantage of all PBBAz is their low compression strength. Modification of the basic chains of their macromolecules and the introduction of bulky substituents into macromolecules were undertaken in order to enhance this parameter, to improve the solubility of PBBAz and to impart specific properties to these systems.

Thus the *p*-phenylene residues of terephthalic acid in the basic chains of PBBAz were replaced by thiophene-2,5-diyl,[47–49] fluorene-2,7-diyl,[50] adamantanediyl,[51] bicyclo[2.2.2]octanediyl [52,53] and 2,2′-bipyridinediyl [54] fragments. In particular, the reaction of the 2,5-diaminobenzene-1,4-dithiol dihydrochloride (**4c**) with thiophene- (**5a**), bithiophene- (**5b**) and terthiophenedicarbonyl (**5c**) dichlorides afforded PBBT **6** soluble in methanesulfonic and sulfuric acids.[47]



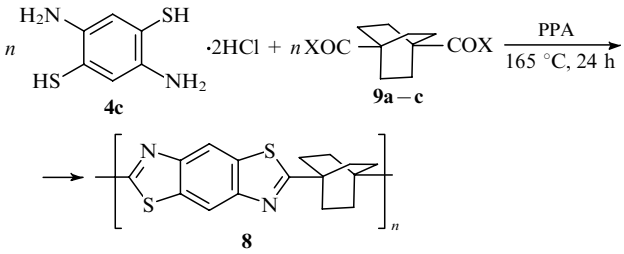
m = 1 (**5a**), 2 (**5b**), 3 (**5c**).

A similar approach was used for the synthesis of a thiophene-containing PBBO.[49] Although PBBT and PBBO are characterised by much lower values of the Kuhn segment than those of the analogous polymers based on terephthalic acid, the majority of their solutions in various acids manifest liquid-crystalline properties.

A certain deviation from a strictly straightened chain was also observed in the case of PBBT **7** prepared from the dihydrochloride **4c** in PPA after partial substitution of fluorene-2,7-dicarbonyl dichloride for the terephthaloyl dichloride (Scheme 1).[50]

Polycyclocondensation at 165 °C results in the formation of high-molecular-weight polymers which are completely soluble in methanesulfonic and sulfuric acids. At higher temperatures, this reaction is accompanied by the formation of insoluble polymers which can be due to the five-membered ring opening in the fluorene fragment.

The colourless PBBT **8** was obtained by the reaction of the dihydrochloride **4c** with bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**9a**), its dimethyl ester (**9b**) or the dichloride (**9c**) in PPA.[52,53]



X = OH (**9a**), OMe (**9b**), Cl (**9c**).

The resulting polymer is soluble in methanesulfonic and sulfuric acids. In terms of thermal stability, the rupture strength and modulus of elasticity, the polymer **8** ranks below PBBT **3** based on terephthalic acid but considerably surpasses it in compression strength.

Poly(benzobisoxazoles) and poly(benzobisthiazoles) containing 2,2′-bipyridinediyl residues were obtained by the reaction of 2,2′-bipyridine-4,4′- or -5,5′-dicarboxylic acids with various mononuclear diaminodiols and diaminodithiols (Scheme 2).[54]

The 4,4′-substituted PBBAz **11** and **12** are soluble in methanesulfonic, sulfuric, trifluoroacetic and formic acids as well as in a mixture of nitromethane with $AlCl_3$. They form strong films. The 5,5′-substituted polybenzazoles **13** and **14** are soluble only in methanesulfonic acid and in a mixture of nitromethane with $AlCl_3$. The solutions of PBBAz **14** form lyotropic mesophases in methanesulfonic acid.

The poly(benzobisazoles) **12a**,**b** and **13a**,**b** manifest extremely high thermal stabilities in inert media and in air (Table 2).

Table 2. Some characteristics of the PBBAz **12** and **13**.[54]

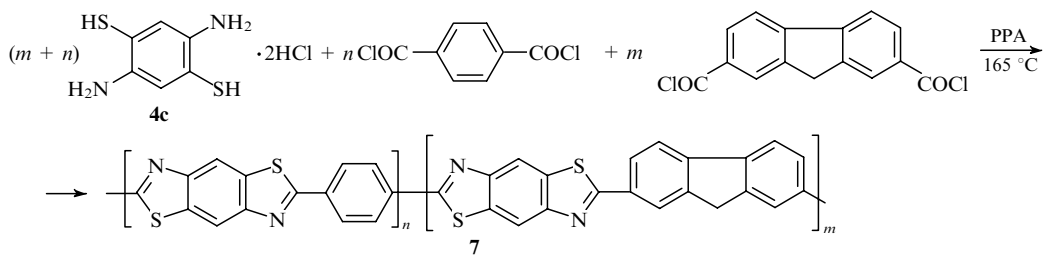
Compound	η_{log} (see [a])	T_{destr} /°C		Yield (%)
		in air	in N_2 atmosphere	
13b	3.1	591	668	82
13c	3.7	537	585	83
12b	1.7	586	648	86
12c	2.1	569	597	87

[a] $MeSO_3H$, 30 °C, c = 0.25 g dl^{-1}.

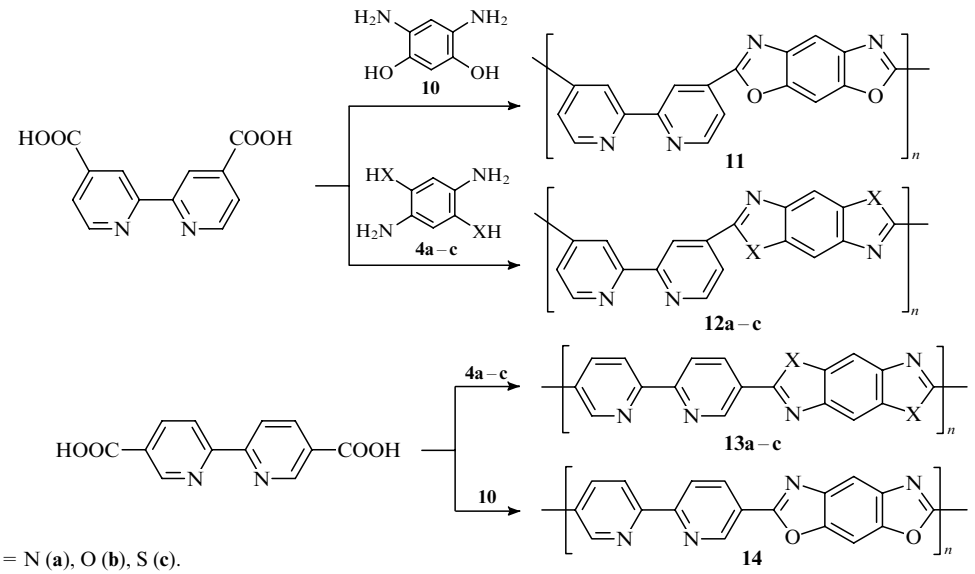
The synthesis of the phenyl-substituted poly[benzo(*N*-phenyl)bisimidazole] **15** [55,56] was carried out in two steps. In the first step, 4,6-dianilinobenzene-1,3-diamine **16** reacted with terephthaloyl dichloride in *N*-methylpyrrolidone (NMP); in the second step, the poly(dianilino)amide **17** formed is cyclodehydrated in PPA to PBBAz **15**.

Poly[benzo(*N*-phenyl)bisimidazole] **15** is one of the first rigid-rod PBBAz. It is soluble in methanesulfonic, sulfuric and formic

Scheme 1



Scheme 2

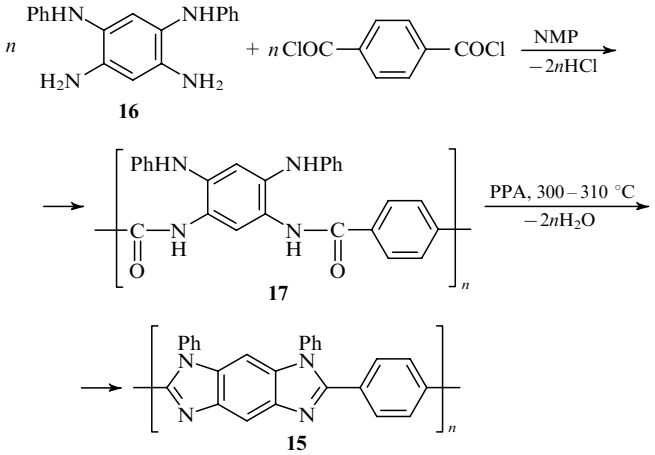


X = N (**a**), O (**b**), S (**c**).

acids as well as in a tetrachloroethane – phenol mixture (3 : 1). This corroborates the hypothesis [57] that the phenyl substituents in the heterocyclic fragment improve the solubility of polyheteroarylenes.[57]

The polymer **15** has a specific viscosity of 9.9 dl g^{-1} and a glass transition temperature (T_g) at 380 °C; at 450 °C, it loses 5% of its mass. Casting of the polymeric solutions was used to obtain films with a rupture strength of 135 MPa.

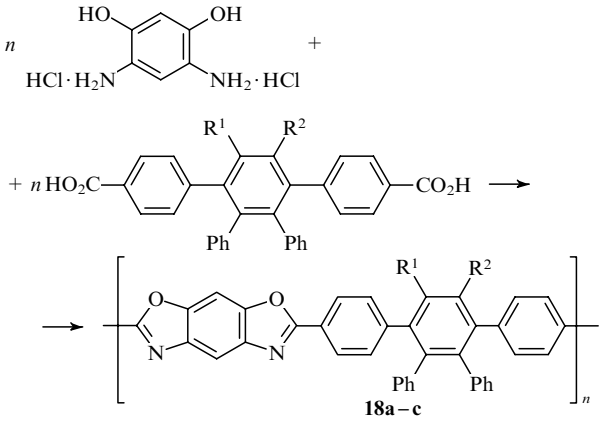
It should be noted that in contrast to other PBBAz, poly-[benzo(*N*-phenyl)bisimidazole] **15** is not formed by direct reaction of 4,6-dianilinobenzene-1,3-diamine **16** with terephthalic acid or its dichloride in PPA.



Much attention has been given to the synthesis of PBBAz with bulky substituents in the carbocyclic fragments of the macromolecules. Such structures are usually synthesised by polycyclocondensation of dicarboxylic acids or their derivatives containing the corresponding substituents.

Wolfe and Arnold [27] were among the first who have synthesised PBBO **18a** – **c** based on di-, tri- and tetraphenyl-*p*-terphenyldicarboxylic acids.

The solubilities of the phenyl-substituted polymers **18a** – **c** exceeds markedly that of the unsubstituted PBBO. In addition to methanesulfonic and chlorosulfonic acids, they are soluble in benzenesulfonic acid and a 7 : 3 mixture of *m*-cresol with dichloroacetic acid as well as in a 9 : 1 mixture of dichloroacetic acid with methanesulfonic acid.



$R^1 = R^2 = H$ (**a**), $R^1 = H$, $R^2 = Ph$ (**b**), $R^1 = R^2 = Ph$ (**c**).

An analysis of the thermal stabilities of PBBO **3b** and the polymer **18b** containing a triphenyl-substituted central fragment revealed that the latter is more resistant to isothermal ageing at 316 °C than PBBO **3b**, but is decomposed more rapidly at 371 °C (Fig. 4) due to the splitting of the phenyl groups.

The poly(benzobisoxazoles), poly(benzobisthiazoles) and poly(benzobisimidazoles) **19a** – **f** containing benzooxazol-2-yl or benzothiazol-2-yl substituents in the phenyl fragment were obtained using the corresponding substituted terephthalic acids **20**.[58 – 61]

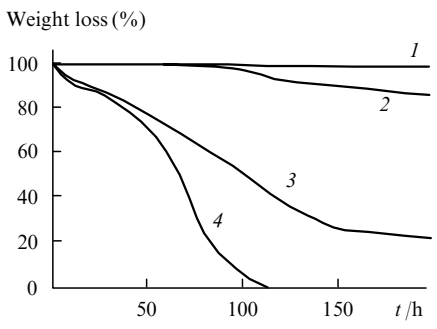
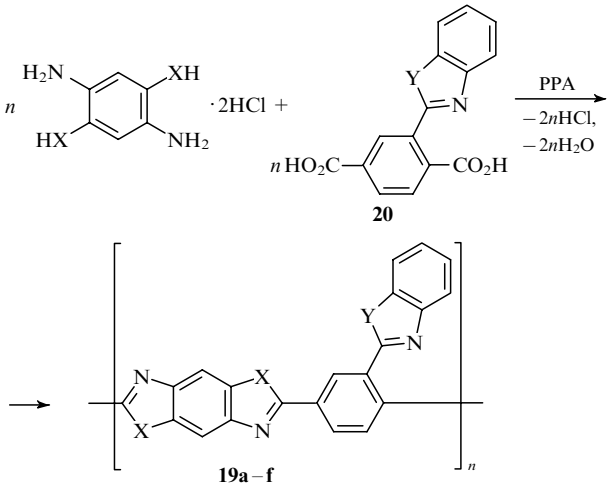


Figure 4. Isothermal ageing of PBBO **3b** and the polymer **18b** powders in circulating air;[27] (*1*) polymer **18b** at 316 °C, (*2*) PBBO **3b** at 316 °C, (*3*) PBBO **3b** at 371 °C, (*4*) polymer **18b** at 371 °C.



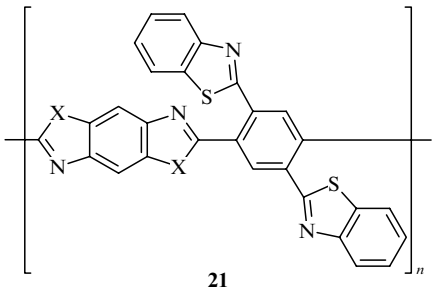
20

19a – f

X = Y = O (**19a**); X = O, Y = S (**19b**); X = Y = S (**19c**);
X = S, Y = O (**19d**); X = NH, Y = O (**19e**); X = NH, Y = S (**19f**).

The PBBAz **19a – f** thus formed were soluble in sulfuric and methanesulfonic acids; the specific viscosities of their solutions in methanesulfonic acid varied from 4 to 19 dl g^{-1}. The anisotropic polymeric solutions (10%, w/w) were used to obtain fibres. The fibres from PBBT **19c** manifested the most valuable properties, *viz*., stability of 2.4 GPa and specific modulus of elasticity of 172 – 207 GPa. Their compression strengths (380 MPa) exceed that of the unsubstituted PBBT **3c**.

2,5-Di(benzothiazolyl)terephthalic acid was used together with 2-benzoazolylterephthalic acids **20** in the synthesis of PBBAz, which afforded PBBAz **21**.[61]



21

Dicarboxylic acids **22a – d** were used as acid components in the synthesis of PBBT and PBBO in order to achieve an even greater disturbance of the close packing of PBBAz and to increase the compression strength.[62, 63]

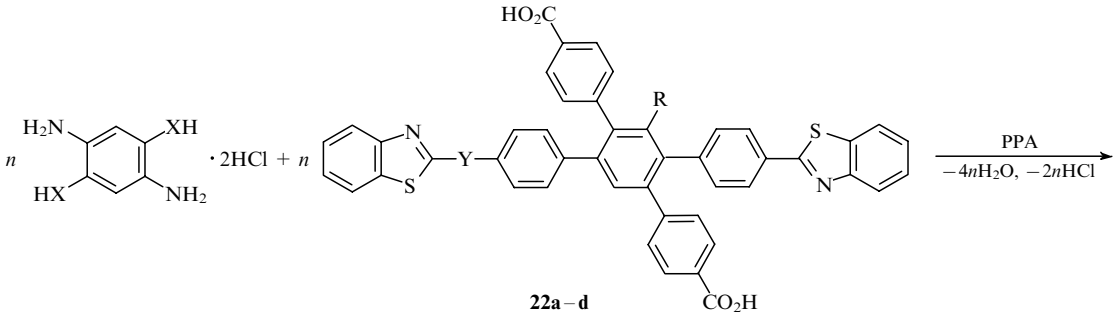
It should be noted that high-molecular-weight PBBAz **23a – d** were obtained only in those cases where polycyclocondensation was carried out at very low concentrations of the monomers in PPA ($\leqslant$ 1%), whereas with an increase in their concentration to 10% only low-molecular-weight oligomers could be isolated from their solutions (Scheme 3).[62]

The poly(benzobisazoles) **23a – d** are soluble in sulfuric, methanesulfonic and trifluoromethanesulfonic acids. The intrinsic viscosities, [η], of the polymers **23a – d** measured in methanesulfonic acid at 30 °C were equal to 12.0, 7.7, 11.4 and 8.7 dl g^{-1}, respectively.

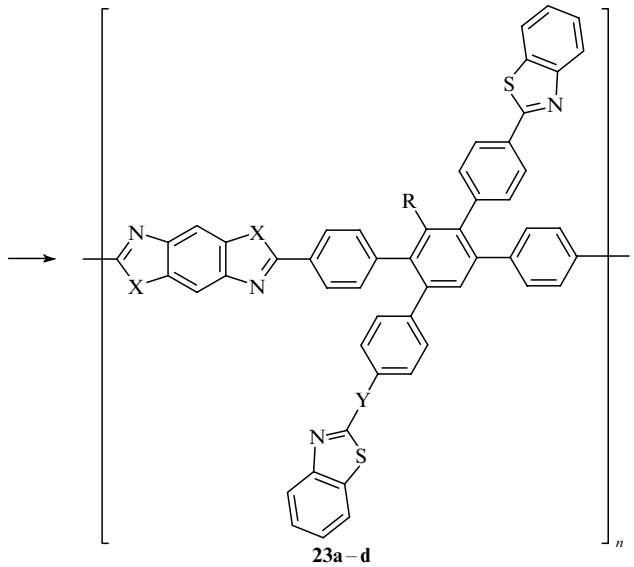
The presence of extended side groups in the PBBAz synthesised prevents the straightening of the basic chains of the macromolecules and the formation of anisotropic solutions as a result of which the attempt to prepare high-quality fibres based on them failed.

The introduction of insignificant amounts (1 mol.% – 2 mol.%) of benzothiazolylphenyl-substituted *p*-terphenyldicar-

Scheme 3



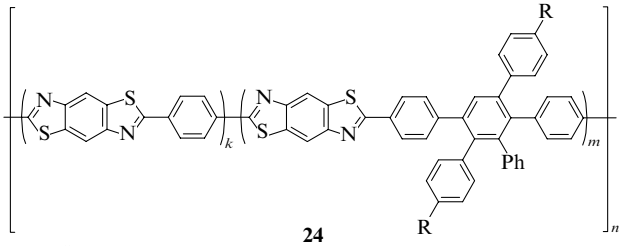
22a – d



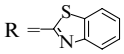
23a – d

Compound **23**	X	R	Y
a	S	Ph	absent
b	O	Ph	"
c	S	H	O–
d	O	H	O–

boxylic acid as a co-monomer to terephthalic acid results in the copolymers **24**.[64]

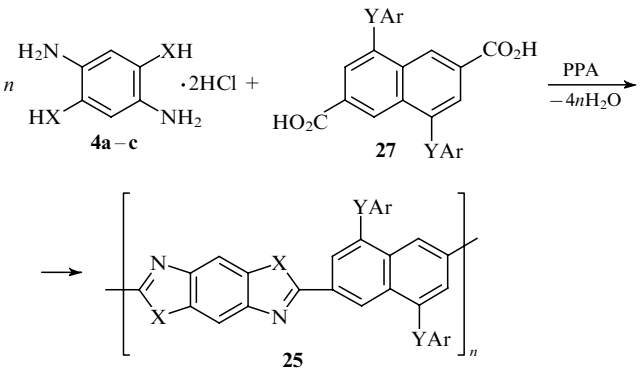


24

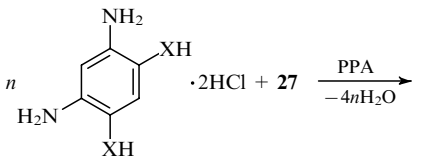


The polycyclocondensation at the concentrations of 10% (w/w) yielded copolymers with intrinsic viscosities of 20 to 28 dl g^{-1}. The fibres prepared from the copolymers **24** manifested a specific strength of 2.5 GPa, a modulus of elasticity of 193–283 GPa and compression strengths of 344 to 482 MPa.

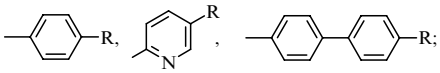
The poly(benzobisazoles), *e.g.*, **25** and **26**, with aryloxide and arylthio substituents were obtained[65] by the reactions of 4,6-diaminoresorcinol, 2,5-diaminohydroquinone-, 4,6-diaminobenzene-1,3-dithiol and 2,5-diaminobenzene-1,4-dithiol hydrochlorides with 4,8-diaryloxy(arylthio)naphthalene-2,6-dicarboxylic acids in PPA.[65]



4a–c **27** **25**



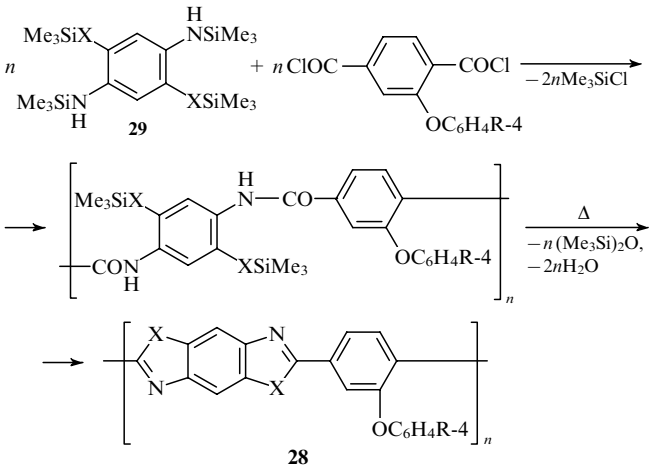
26

X = O, S, NH; Ar = 

R = H, Me, Et, Pr^n, Pr^i; Y = O, S.

In addition to a single-step synthesis of PBBAz in PPA, two-step synthetic procedures have been developed which yield prepolymers in the first stage under mild conditions. Their subsequent solid-phase cyclisation yields poly(benzobisazoles).

Thus the polymers **28** which are soluble in mixtures of dichloromethane chloride with methanesulfonic and trifluoroacetic acids have been synthesised from the silyl derivatives **29** and aryloxy-substituted terephthaloyl dichlorides by Kricheldorf *et al.*[66–70]

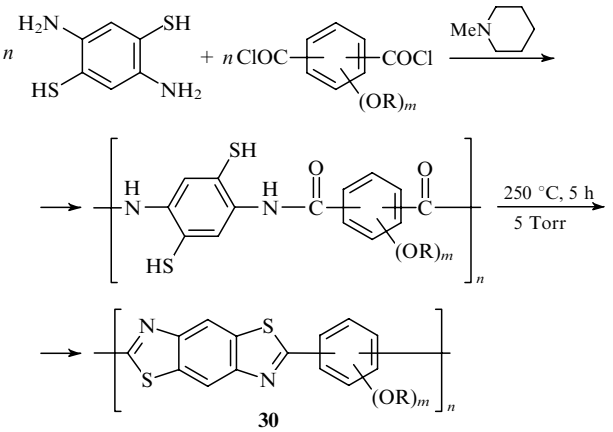


29 **28**

X = O, S; R = Ph, OPh, Bu^t, Cl, Br.

The use of silylated monomers makes it possible to increase the nucleophilicity of the nitrogen atom, as a result of which the reaction with acid chlorides proceeds more selectively and does not affect the trimethylsilyloxy(thio) groups.[71–74]

Kimura *et al.*[75] used a stepwise procedure for the synthesis of the alkoxy-substituted PBBT **30**.



30

R = Bu^n, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$; m = 1, 2.

Nearly all the PBBT **30** were able to form anisotropic melts in the temperature range from 280 to 450 °C.

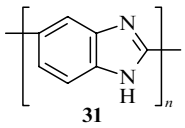
On the whole, it should be noted that most PBBAz can successfully be used for the preparation of high-quality fibres and films; however, bulk products can hardly be obtained, since their glass transition temperatures exceed their decomposition temperatures. This problem was solved, to a large extent, within the framework of a new concept in materials technology, namely, the construction of molecular composites.[76]

III. Molecular composites

The term molecular composites is usually applied to describe systems which consist of rigid-rod molecules dispersed in matrices of flexible-rod molecules at the molecular level; in this case, rigid-rod molecules play the role of reinforcing elements.

Molecular composites can be prepared both by mixing rigid- and flexible-rod polymers at the molecular level and by synthesising block and graft copolymers containing rigid- and flexible-rod fragments.

Among the first molecular composites were those based on PBBT **3c** as a rigid-rod component and polybenzoimidazole (**31**, ABPBI) as a flexible-rod component.[77–79]



31

Poly(benzoimidazole) (**31**) was obtained by homocondensation of 3,4-diaminobenzoic acid in PPA.[80,81]

Mixtures of these polymers at the molecular level were prepared from solutions with concentrations below those required for precipitation.[78,79] The mechanical properties of PBBT – ABPBI molecular composites (both as fibres and as films) are listed in Table 3. As can be seen from the Table 3, the introduction of 30% PBBT into the matrices of ABPBI enhances significantly the deformation strength characteristics of the material. The results of morphological studies of these mixtures, *viz*., low- and wide-angle X-ray scattering, optical microscopy and scanning electron microscopy suggest the absence of phase separation.[77,82,83]

Table 3. Mechanical characteristics of fibres and films based on the PBBT – ABPBI molecular composites.

Composite	Product	E/GPa	σ/MPa	ε(%)	Ref.
PBBT	fibre	300	3000	1.1	82
ABPBI [a]	"	16.8	675	29	77
ABPBI [b]	"	36.0	1110	5.2	82
PBBT – ABPBI					
(30 : 70) [a]	"	16.8	1161	7.2	77
see [c]	"	71.7	1215	2.5	77
see [d]	"	109.7	1283	1.8	77
PBBT – ABPBI					
(30 : 70) [a]	film	30.4	690	55	83
see [e]	"	88.2	918	2.4	83

[a] Freshly formed; [b] heat-treated; [c] heat-treated at 427 °C; [d] heat-treated at 525 °C; [e] heat-treated at 540 °C.

The processability of molecular composites could be improved using thermoplastic polymers, *e.g*., amorphous and partially crystalline polyamides,[84,85] poly(phenylquinoxalines)[86] and poly(ether ether ketones)[87] as flexible-rod matrices. The mechanical characteristics of the molecular composites based on thermoplastic polymers and PBBT are listed in Table 4. Thus the mechanical properties of the PBBT – Nylon system exceed those of a monoaxially oriented fibrous composite with identical composition by 50% – 300%.

As well as the construction of composites at the molecular level, the design of molecular composites by the synthesis of block and graft copolymers has become a very popular approach. Whereas in the molecular composites prepared by mechanical mixing of flexible- and rigid-rod components the reinforcing

Table 4. Mechanical characteristics of PBBT – thermoplastic molecular composites.

Thermoplastics	Composition (w/w)	Product	E/GPa	σ/MPa	Ref.
Poly(phenylquinoxaline)	30 : 70	fibre	17.5	355	86
Nylon	30 : 70	"	36.0	345	86
Poly(ether ether ketone)	50 : 50	film	11.0	248	87
		block	15.8	105	87
Nylon-6,6	50 : 50	"	20.8	183	85

macromolecules are bound to the matrices exclusively due to physical interactions, in block copolymer-based molecular composites the flexible- and rigid-rod fragments are linked by covalent bonds. As a result, the transfer of strains from the rigid-rod fragments to the flexible-rod matrices occurs more effectively, hence, the block copolymer-based molecular composites manifest higher deformation strengths and dimensional stabilities.

The block copolymers **32** of the ABA type[88] which contain rigid-rod blocks B and flexible-rod blocks A[88] were synthesised as model systems. Macromolecules of PBBT **33** with carboxy terminal groups ($[\eta] = 10-24$ dl g^{-1}) used as rigid-rod blocks were introduced into co-polycondensation with 3,4-diaminobenzoic acid hydrochloride, which resulted in the formation of benzoimidazole rings and simultaneous binding of the individual blocks (Scheme 4).

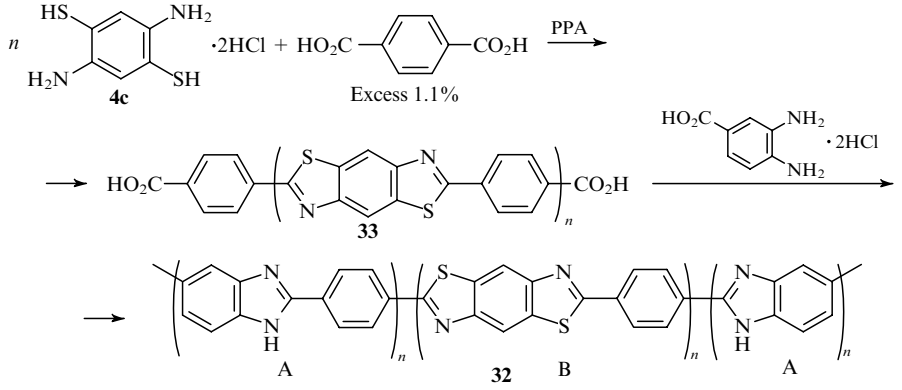
The compositions of the blocks were varied by changing the content of 3,4-diaminobenzoic acid used for co-polycondensation. As can be seen from Table 5, the moduli of elasticity of the block-copolymeric molecular composites are comparable with those of the dynamic mixtures; their magnitudes depend on the ratios of the rigid- and flexible-rod components. The values of the moduli suggest that the reinforcement does not necessarily require highly extended macromolecules of PBBT **32**. Comparison of the breaking strengths (see Table 5) points to a much higher (up to

Table 5. Some characteristics of the block copolymers and mixed molecular composites.[88]

Ratios [a]	$[\eta]$/dl g^{-1}		E/GPa	σ/MPa	ε(%)
	PBBT **32**	copolymer			
30 : 70	10.7	8.5	102.7	1696	2.3
25 : 75	12.9	10.7	94.5	1566	2.5
30 : 70	17.7	7.3	115.8	1600	1.4
30 : 70	see [b]	see [b]	116.5	1268	1.4

[a] The PBBT **32** : ABPBI **31** ratios for the copolymer; [b] a physical mixture comprising 30% (w/w) PBBT **32** ($[\eta] = 31$ dl g^{-1}) and 70% (w/w) ABPBI **31** ($[\eta] = 17.6$ dl g^{-1}).

Scheme 4



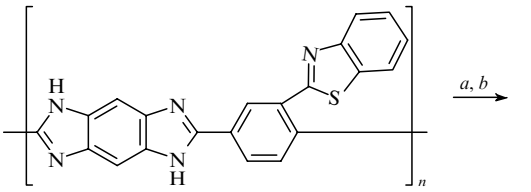
33%) deformation strength of the block-copolymeric molecular composites compared with the materials prepared from mechanical mixtures.

The polybenzobisthiazoles carrying terminal carboxy groups were introduced into the Friedel–Crafts polycondensation reaction with *m*-phenoxybenzoic acid in a P_2O_5–$MeSO_3H$ mixture.[89] This reaction yielded block copolymers of the ABA type which contained flexible-rod polyether ketone blocks and rigid-rod PBBT blocks.

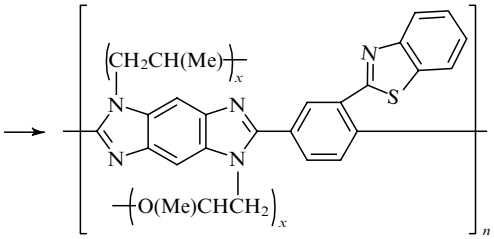
In addition to block-copolymeric molecular composites, much attention has been given to the synthesis of molecular composites based on graft copolymers containing rigid- and flexible-rod macromolecules. In particular, benzothiazol-2-yl-substituted PBBI **34** was metallated using NaH in DMSO with subsequent treatment with acrylamide[90] or, which is especially important, with propylene oxide.[90–92]

The grafted copolymer **35** is soluble in methanesulfonic, 97% formic and trifluoroacetic acids much more easily than PBBI **34**.

Although the softening of these polymers could not be detected by differential scanning calorimetry, their solid melts could be obtained by compaction at 190–232 °C. The introduction of polypropylene oxide side chains is accompanied by a significant decrease in their thermal stabilities in comparison with that of the starting compound, *viz*., PBBI **34**.



34



35

(*a*) NaH, DMSO, (*b*) Me–CH(O)–CH_2.

Of special interest is the synthesis of molecular composites based on grafted copolymers with heat-resistant side chains. Since rigid-rod PBBAz are soluble only in acidic solvents, the set of reactions used for the grafting is rather limited. Evers *et al.*[93,94] used the Friedel–Crafts reaction of *m*-phenoxybenzoic acid with poly(benzobisthiazole) in $MeSO_3H$–P_2O_5 (10 : 1, w/w) for the synthesis of grafted copolymers of the AB type. Thus the reaction of the polybenzobisthiazole copolymer **36** containing 4,4′-(*o*-diphenoxyphenylene) groups which are distributed statistically among the fragments of the rigid-rod PBBT with *m*-phenoxybenzoic acid afforded the copolymer **37** (Scheme 5).[95]

Compaction at high temperatures and pressures (285 °C, 6.9 MPa) is employed for the preparation of bulk products possessing isotropic properties. The main disadvantage of this approach is the low elasticity of the grafted fragments.

An alternative approach is based on the use of polybenzobisthiazole copolymers containing 2,6-dimethylphenoxide side groups as the basic macromolecular chains.[96,97] Treatment of these systems with *m*-phenoxybenzoic acid in P_2O_5–$MeSO_3H$ was accompanied by the formation of the grafted copolymers **38** (Scheme 6).

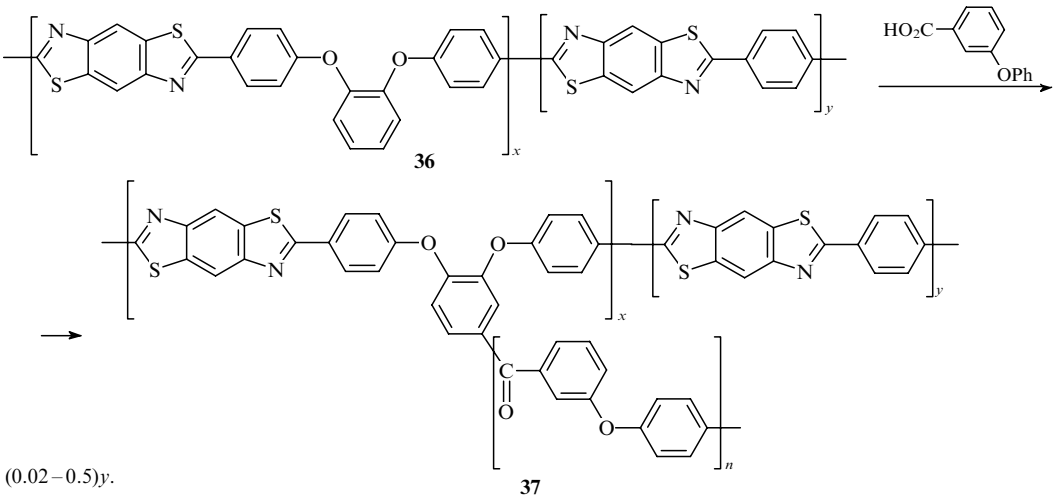
According to the dynamic mechanical analysis data, the softening of the grafted copolymers **38** occurs at 180–265 °C depending on the value of y.[98] Their secondary processing into bulk products is carried out at pressures up to 40 MPa and at temperatures which are 40 to 50 °C higher than the softening temperature. A specimen containing 46% (w/w) of PBBT **3c** and 54% (w/w) of the copolymer **38** manifests a rupture strength of 40 MPa and modulus of elasticity of 9.7 GPa.

IV. Conclusion

Rigid-rod PBBAz are the most promising materials in those fields where small weight, high deformation strength, rigidity, thermal and chemical stability as well as radiotransparency are the critical factors. The latter property is especially important, and in this respect PBBAz fibres have an indisputable advantage over graphite fibres. PBBAz fibres manifest greater elongation at rupture in comparison with graphite fibres and possess higher thermal and thermooxidative stabilities in comparison with Kevlar fibres. This altogether demonstrates their usefulness for aeronautical, aerospace and electronic engineering. Yet another field of application in which PBBAz have obvious advantages over glass, Kevlar fibres and coal plastics are thermostable membranes and filters. Further progress in this area will largely depend on the cost of the monomers and the 'cost–property' ratios of these systems.

The main drawback of the materials based on PBBAz is their low compression stability. This review considers the individual approaches to the solution of this problem which are based on structural modifications of these polymers. In recent years, increasing attention has been given to the construction of

Scheme 5

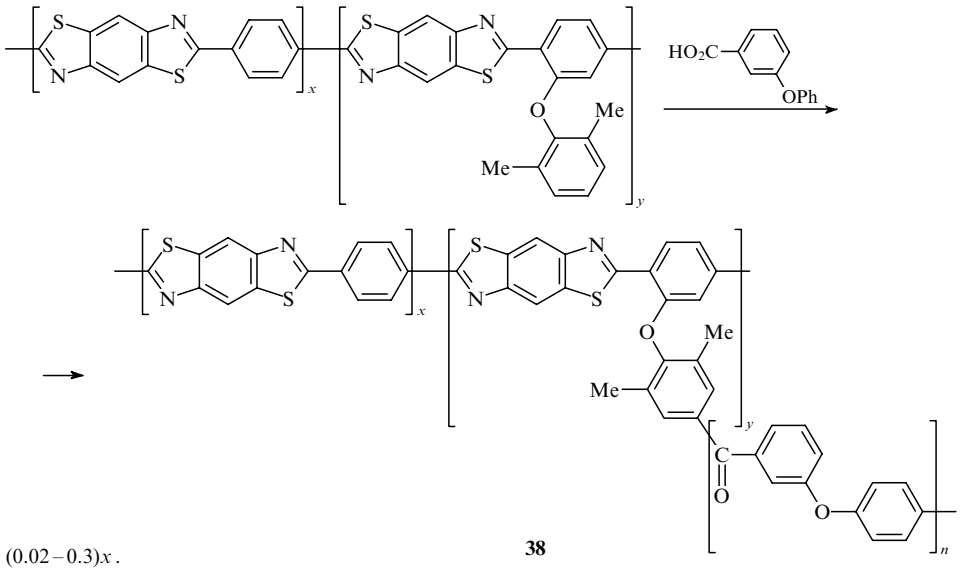


36

37

$x = (0.02–0.5)y$.

Scheme 6



$y = (0.02-0.3)x$.

38

PBBAz that can be cross-linked to form three-dimensional structures.[99–101] Further developments in this field will obviously be aimed at the construction of systems whose solidification is not accompanied by the evolution of volatile by-products.

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