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Polymeric Derivatives of Adamantane

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The literature data on the synthesis and properties of polymers with fragments of the polyhedral structures of adamantane and 1,1'-biadamantane are surveyed. The inter-relation between the structures of the polyhedral monomers and their reactivities is examined. A distinctive feature of the adamantane-containing polymers, together with their high thermal stability, is their resistance to hydrolysis and oxidation and to the action of light and solvents.
The bibliography includes 114 referenees.

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I. INTRODUCTION

Compounds with a polyhedral structure have attracted the attention of investigators from the standpoint of the possibility of obtaining polymers with valuable practical properties. An example of this is provided by the carbaborane-containing polymers the methods of synthesis of which are based on the functional transformations of carbaboranes—polyhedral systems with a boron–carbon skeleton[1].

One of the "growth points"[2] in organic chemistry at the present stage consists of studies in the field of polyhedral hydrocarbons and in the first place adamantane, first detected in petroleum by Landa[3] in 1933. These studies developed further after Schleyer et al.[4] achieved the isomerisation of tetrahydrobicyclopentadiene to adamantane in the presence of aluminium halide. The ease of this rearrangement can be accounted for by the high thermodynamic stability of adamantane; treatment of all the known $C_{10}H_{16}$ isomers with Lewis acid inevitably leads to this tricyclic hydrocarbon[5]. The antiviral activity of 1-aminoadamantane hydrochloride was discovered in 1964.[6] Since then there has been a continuous growth of the number of studies on adamantane and related polyhedral hydrocarbons; they have been surveyed in a whole series of reviews[7-19]. Certain special fields concerning heteroadamantanes[20,25] and the pharmacological activity of adamantane derivatives[21,22] have been examined. The first monograph on adamantane has been published recently[22].

Fairly numerous studies, described mainly in patents, have been made on polymeric adamantane derivatives. However, if one disregards a brief review on adamantane polymers[23] quoting four original communications, the literature on this field has not been surveyed. At the beginning of 1977 a review was published[24] on the structure and stereochemistry of adamantanoid hydrocarbons in which certain problems of the stereochemistry of polyadamantanes—low-molecular-weight linear polymers—were examined together with those concerning higher adamantane homologues. Studies on silicon-containing polymeric derivatives of adamantane have been described in a review[25].

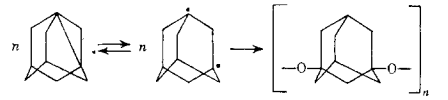
II. CARBOCHAIN POLYMERS OF ADAMANTANE

Polyadamantane was obtained for the first time[26] from 3,3'-dibromo-1,1'-biadamantane by the Wurtz reaction:



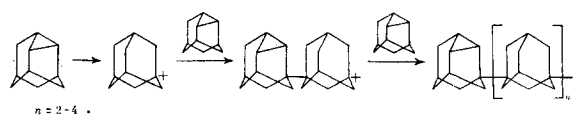
The polymer (melting point above 420 °C) was a white powder insoluble in the usual organic solvents and resistant to the action of concentrated hydrochloric acid and 5 *N* solution of alkali. According to X-ray diffraction data, the polyadamantane had a degree of crystallinity in excess of 80%.

Dehydroadamantanes may serve as another source of polyadamantane. 1,3-Dehydroadamantane is an extremely reactive compound; on heating to 130–160 °C, it is converted into a solid polymer without fusion[27]. In solutions in the presence of atmospheric oxygen 1,3-dehydroadamantane forms an adamantane polyperoxide with opening of the inner cyclopropyl ring even at room temperature[28]:



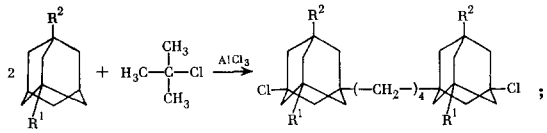
On heating, the polyperoxide decomposes explosively in the temperature range 146–180 °C.

Polyadamantane is also formed on polymerisation of 2,4-dehydroadamantane under the influence of aluminium chloride[29]. The reaction proceeds via a stage involving the formation of the adamantyl cation and subsequent hydride transfer from 2,4-dehydroadamantane:



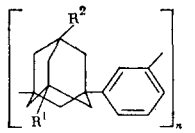
Interesting results have been obtained in the polycondensation of polybromoadamantanes under the influence of metallic sodium[30]. The product is a three-dimensional carbon polymer and consists of the carbon nuclei of adamantane. It consists of a white powder with a carbon content of ~ 99% and a density of 2 g cm^{-3}. It is insoluble in organic solvents.

Oligomers consisting of two and three adamantane nuclei and short methylene chains between them have been obtained by the polycondensation of adamantane and its homologues with alkyl halides in the presence of $AlCl_3$ or $AlBr_3$.[31] An example is provided by the reaction between alkyladamantane and t-butyl chloride:



R^1 and R^2 = CH_3, or C_2H_5

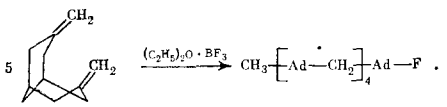
The process takes place at 20–30 °C in the course of 1 h. The number of nuclei in the chain can be increased by employing a large excess of the initial adamantane homologue. The copolymers of adamantane and benzene can serve as another example of mixed polyadamantanes[32]:



where R^1 and R^2 = alkyl and n = 9–10.

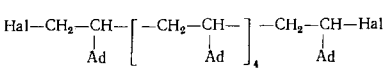
The reaction of alkyladamantane with di-t-alkylbenzenes takes place in the presence of Lewis acids at temperatures between 0° and +25 °C for equimolar reactant ratios. The resulting polymer with a molecular weight of 2300 is a solid, which melts at 250 °C and forms protective films and coatings with a high resistance to thermal oxidation[32].

Polyadamantane with methylene bridges in the chain is a product of the cationic polymerisation of 3,7-bismethylenebicyclo[3.3.1]nonane in an organic solvent (n = 4)[33]†:

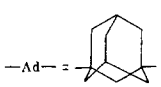


The polymer is insoluble in organic solvents and melts above 340 °C.

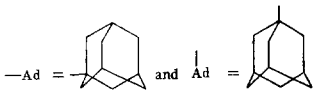
Certain polymers of vinyl derivatives of adamantane are known. Under the influence of $AlCl_3$ or $AlBr_3$ in methylene chloride, vinyladamantane gives rise to a solid product which is insoluble in organic solvents[34]. On the basis of the results of elemental analysis, a formula has been proposed for the oligomer#:



† Here and henceforth



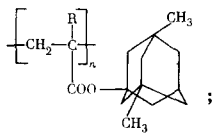
Here and henceforth



The homopolymer of 1-allyladamantane and its copolymer with vinylcyclohexane have been obtained by polymerisation in the presence of a complex catalyst—(iso-BuO)$_3$Al–$TiCl_4$.[35] However, no information about the properties of these polymers is presented in the relevant communication.

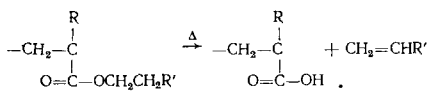
Adamantyl acrylates and methacrylates polymerise under the influence of free-radical and anionic catalysts[36,37] and also under ultraviolet irradiation[38].

The study of the kinetics of the radical polymerisation showed that both the methacrylates and the vinyl esters of adamantane derivatives are highly reactive[39], i.e. the adamantyl group does not inhibit polymerisation. The principal distinctive properties of such polymers are high glass points, considerable surface hardness, brittleness and low mechanical strength, and insignificant contraction on polymerisation. These properties are due to the presence in the macromolecules of the bulky adamantyl group, which increases the rigidity of the polymer chains:



R = H, or CH_3.

One of the causes of the thermal degradation of polyacrylates is the cleavage of the ester side-groups with formation of an olefin:

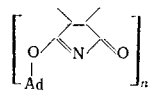


The reaction does not occur for poly(adamantyl acrylates) and this is a particular reason for their high thermal stability.

Solutions of poly(adamantyl acrylates) are very viscous, which led to their use as thickening agents for lubricating oils[38]. For example, a 1% solution of poly(dimethyladamantyl acrylate) with a molecular weight of 80000 has the same viscosity as a 2% solution of poly(methyl methacrylate) with a molecular weight of 117000.

Acrylate and methacrylate esters of adamantanols copolymerise with methyl methacrylate, styrene, acrylonitrile, and vinyl chloride[37]. The properties of the copolymers depend on their composition, but in all cases copolymerisation with adamantyl acrylates leads to an increase of the glass points and of the hardness of the copolymers.

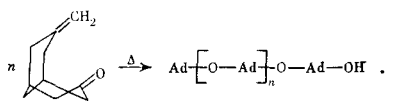
The influence of bulky substituents on the stereoregularity of the polymers of vinyl ethers and esters has been studied[42]. Investigation of the infrared spectra of the polymer films showed that the adamantyl group promotes a high syndiotacticity of the poly(vinyl carboxylate) and the isotacticity of the vinyl ether. The orienting effect of the adamantyl group is similar to that of the t-butyl group, which can be regarded as the open-chain analogue of the adamantyl group. Like adamantyl methacrylates, poly(adamantyl vinyl ethers) have high softening temperatures (210–225 °C). The homo- and co-polymerisation of the heterocyclic derivative 5-(1′-adamantyloxy)-2H, 2-pyrrolone with various vinyl monomers have been studied in detail[43]. Spectroscopic investigations have shown that the polymerisation takes place as a result of the partial dissociation of the C=C bond in the heterocycle:



The presence of the pyrrolone heterocycle in the polymer chain led the authors[43] to investigate the photochemical properties of the polymer films. It was found that, on ultraviolet irradiation, photochemical transformations, accompanied by the formation of cyclopropyl isocyanate groups, take place in the polymer. The copolymers of 5-(1′-adamantyloxy)-2*H*, 2-pyrrolone are characterised by an alternation of the comonomer units and the high values of the parameters $Q = 3.40$ and $e = 1.59$ indicate, according to the authors, electron-accepting properties of the substituent—the adamantyl group. The homo- and co-polymers of 5-(1′-adamantyloxy)-2*H*, 2-pyrrolone have high glass points (220–245 °C). On thermolysis of the homopolymer, the adamantyl group migrates to the nitrogen atom with formation of poly-*N*-(1-adamantyl)maleimide.

III. POLYETHERS, POLYESTERS, POLYSULPHONES, AND POLYCARBONATES OF ADAMANTANE

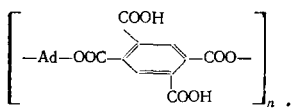
The polyether may have been the first polymeric heterochain derivative of adamantane obtained[44]. In their study of the possibility of synthesising the adamantane nucleus from bicyclic systems, Stetter et al.[44] observed that, when 3-methylenebicyclo[3.3.1]-7-nonanone is heated in an inert solvent in the presence of toluene-*p*-sulphonic acid, a polyether derived from adamantane is formed with a quantitative yield:



Polyethers have been synthesised by the reaction of the phenoxides derived from 1,3- and 2,2-bis(4′-hydroxyphenyl)-adamantanes with di(4-chlorophenyl) sulphone and 4,4′-difluorobenzophenone[45] and also by the reaction of 3,3′-dibromo-1,1′-biadamantane with diphenoxyethane[40,41].

Numerous studies, described mainly in patents[46–55], have been devoted to the synthesis of polyesters based on adamantanedicarboxylic acids or adamantane diols. The starting compounds for the synthesis of adamantane-containing polyesters are either the diesters of adamantanedicarboxylic acids (transesterification with glycols) or the highly reactive chlorides of the corresponding dicarboxylic acids. Calcium acetate–antimony dioxide[40] and sodium hydride–hexabutoxytitanate[41] systems as well as tetraisopropyl titanate and toluene-*p*-sulphonic acid[46–48] can be used as transesterification catalysts. The chloride of adamantane-1,3-dicarboxylic acid is highly reactive. The rate constant for its reaction with diethylene glycol, for example, in the temperature range 100–140 °C varies from 0.0044 to 0.0203 litre mol^{-1} s^{-1}.[56]

The majority of the polyesters have a low molecular weight owing to the steric influence of the adamantane nucleus. This is demonstrated by the esterification of adamantane-1,3-diols by tetracarboxylic acid dianhydrides[51]. If the reaction is carried out in dimethylformamide (DMF) at a low temperature (60 °C) and in the presence of toluene-*p*-sulphonic acid, then a linear non-cross-linked polyester with free carboxy-groups is obtained:



This can be explained by the fact that, in the esterification of the first carbonyl group in one of the anhydride moieties by adamantane-1,3-diol, the bulky adamantyl group causes steric hindrance of the reaction of the second adamantanediol molecule with the carbonyl group adjoining the esterified group. On the other hand, the second anhydride moiety is not sterically hindered and reacts with the diol. This type of polyester is soluble in 5% aqueous sodium bicarbonate solution and can be cross-linked by glycols, di-isocyanates, and other functional compounds and also on heating. Some of the properties of the linear polyesters are presented in Table 1.

Table 1. The properties of adamantane-containing polyesters.

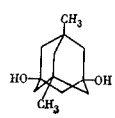
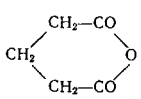
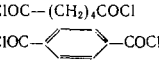
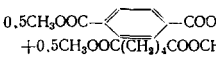
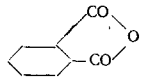
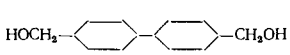
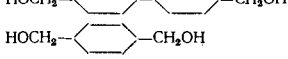
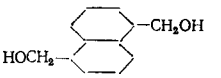
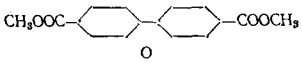
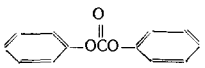
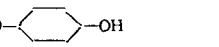
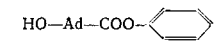
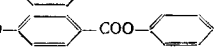
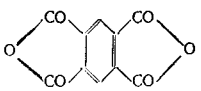
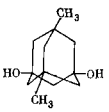
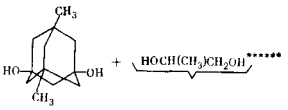
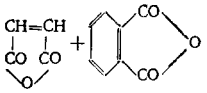
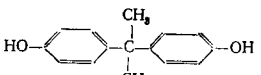
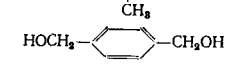
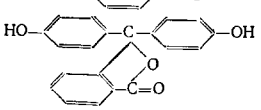
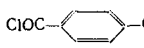
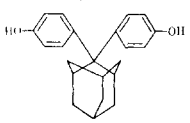
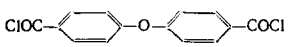
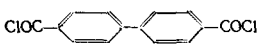
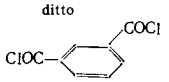
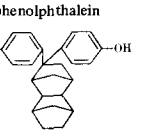
Dicarboxylic acid or its derivative	Diol	(MW)*	t_s^{**}, °C	Characteristics of polymer****	References
$C_2H_5OOCCH_2COOC_2H_5$		0.9 (1616)	99***	solid, brittle	[46, 47, 55]
	ditto	0.25 (4430)	51***	solid, vitreous	[46, 47, 55]
$ClOC-(CH_2)_4COCl$	»	0.08 (925)	12***	viscous liquid	[46, 47, 55]
	»	0.09 (1490)	165***	30% crystallinity	[46, 47, 55]
	»	0.11	160***	—	[46, 47, 55]
	»	0.32	110***	solid, vitreous	[55]
$CH_3OOC-Ad-COOCH_3$	$HO(CH_2)_2OH$	—	—	viscous liquid	[40, 41]
$CH_3OOC-Ad-COOCH_3$	$HOCH_2-Ad-CH_2OH$	0.23	—	*stable on heating* to 325 °C	[40, 41]
ditto		0.25	230	resistant to u.v. light	[40, 41]
»		0.48	170	—	[40, 41]

Table 1 (cont.)

Dicarboxylic acid or its derivative	Diol	η_{ln} (MW)*	t_s^{**}, °C	Characteristics of polymer****	References
$CH_3OOC-Ad-COOCH_3$	$HOCH_2-C_6H_4-CH_2OH$	0,37	250	—	[40, 41]
»		0,20	140	—	[40, 41]
	$HOCH_2-Ad-CH_2OH$	0,30	210	—	[40, 41]
	ditto	0,20	260	—	[40, 41]
ClOC—Ad—COCl		1,0	194—200	stable on heating to 350 °C	[49]
		(17500)	310	—	[50]
$CH_3OOC-Ad-COOCH_3$	$HO(CH_2)_4OH$	—	138***	stable on heating to 350 °C	[52]
		—	—	solid powder soluble in 5% aqueous NaOH	[52]
		—	—	d=1,16; σ_f=32,6	[48]
	ditto ******	—	—	τ_0=305° C; d=1,17; σ_b=67.7	[48]
ClOC—Ad—COCl		0.57*****	300	τ_0=360° C	[53]
ClOC—Ad—COCl		0,45****	230	—	[53]
ditto		0.75****	315	τ_0=350° C	[53]
»	$HO(CH_2)_4OH$	0.33*****	90	—	[57]
		0.51	—	τ_0=420° C, crystalline	[58]
ditto	ditto + bisphenol A	0.82	280	τ_0' = 330 °C, soluble in chloroform, DCE, TCE, and tricresol	[59]
»	ditto + phenolphthalein	0.85	330	τ_0' = 330 °C, soluble in chloroform	[59]
	ditto + bisphenol A	0.90	265	τ_0=340° C, ditto	[59]
ditto	ditto + phenolphthalein	0,58	290	τ_0=340° C, ditto	[59]
	ditto + bisphenol A	0.36	285	τ_0 = 330 °C, soluble in TCE + tricresol mixture	[59]
ditto	ditto + phenolphthalein	0.15	310	τ_0=360° C, ditto	[59]
	ditto + bisphenol A	0.27	260	τ_0=320° C, ditto	[59]
ditto	ditto + phenolphthalein	0,14	300	τ_0=340° C, ditto	[59]
»	ditto + 	0.30	290	τ_0=340° C, soluble in TCE	[59]

* Logarithmic viscosity η_{ln} measured in a phenol (60%)–tetrachloroethane (40%) mixture; the molecular weight (MW) was measured osmometrically in benzene.

** Softening temperature.

*** Reduced glass point (according to thermogravimetric data).

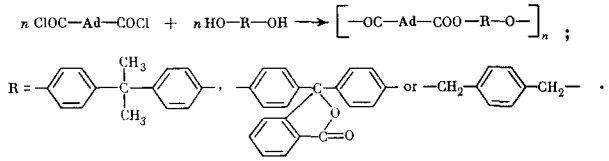
**** Notation: τ_0 = temperature of onset of weight loss; d = density (g cm^{-3}); σ_f = flexural strength (MPa).

***** The intrinsic viscosity η_{int} is given.

****** Hardened with styrene.

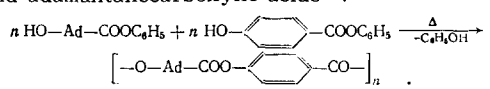
Unsaturated polyesters, which subsequently acquire a structure in the presence of peroxides, can be obtained by the reaction of adamantane-1,3-diol with maleic anhydride. Their composition and properties can be varied within wide limits by adding other dianhydrides, for example, phthalic dianhydride or comonomers—styrene and methyl methacrylate[48].

The polyesterification of the chloride of adamantane-1,3-carboxylic acid by bisphenols in high-boiling solvents[53] or under the conditions of acceptor-catalytic polycondensation in solution[54] leads to adamantane-containing polyesters with a fairly high molecular weight:



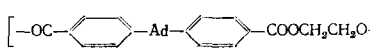
Mixed polyarylates have been synthesised by the high-temperature polycondensation of 2,2-bis(4′-hydroxyphenyl)-adamantane, cardo-bisphenols, and the chlorides of isophthalic and terephthalic acids[58,59]. The polyarylates have a crystalline structure and the degree of their crystallinity depends on the content of adamantane groups.

Mixed polyesters have also been obtained by the joint polyesterification of the phenyl esters of aromatic hydroxy-acids and adamantanecarboxylic acids[50]:



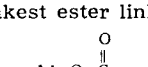
The reaction is carried out under fairly severe conditions (330 °C, 0.3 mmHg) in the presence of dibutyltin as the catalyst.

Thermostable adamantane-containing polyesters, produced by the bulk condensation of 1,3-bis(4′-methoxycarbonylphenyl)adamantane with ethylene glycol, have been described[52]:

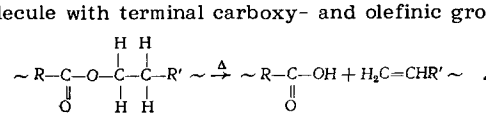


The reaction is carried out under conditions resembling those in the synthesis of poly(ethylene terephthalate). In the first stage at 160 °C and 0.3 mmHg a diglycol ether is obtained and is then gradually heated in the presence of antimony oxide to 245 °C at a pressure of 0.15 mmHg.

Adamantane-containing polyesters have fairly high glass points and softening temperatures (Table 1) and it has been noted in a number of studies[46,47,55] that they are highly resistant to thermal and oxidative degradation and exhibit an effective hydrolytic stability. This is particularly notable when adamantanediol is used. In this case the adamantane nucleus adjoins the weakest ester linkage

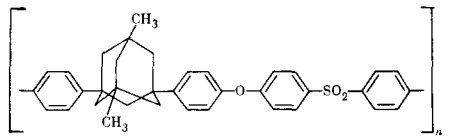


and prevents its being acted upon by hydrolysing agents[46]. In addition one of the ways of decomposing the polyesters involves the elimination of hydrogen from the β-position in the alcoholic residue with formation of two fragments of the macromolecule with terminal carboxy- and olefinic groups:

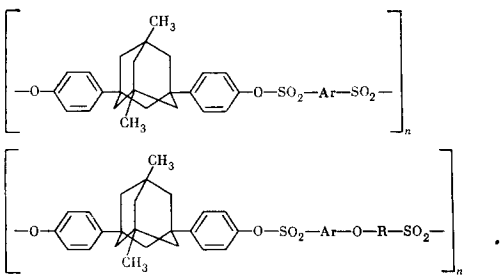


On the other hand, the formation of a double bond in the adamantane nucleus is impossible under these conditions, so that the decomposition of adamantanediol polyesters is difficult[55]. Both linear and cross-linked polyesters are highly resistant to the action of ultraviolet light and sunlight[48]. These properties make adamantane-containing polyesters useful as protective coatings and packing materials.

A whole series of polyesters based on 1,3-bis(4′-hydroxyphenyl)-5,7-dimethyladamantane have been described. The reaction of the latter with di(halogenophenyl) sulphones yielded polysulphones, for example[60]:



The reaction is carried out in an organic solvent in air at 160 °C. A necessary condition is preliminary synthesis of the disodium salt of a bisphenol by the reaction of the latter with an aqueous NaOH solution. Using bisarenesulphonic acid esters or chlorides instead of dihalogenosulphones, one can obtain the corresponding polysulphonates[61,62]:



Triethylamine is used as the HCl acceptor. The reaction takes place fairly rapidly (1—2 h) and yields a high-molecular-weight product with an intrinsic viscosity of 1.1—1.2 dl g^{-1}. In contrast to the usual polysulphonates, the adamantane-containing polysulphones and polysulphonates are rigid and strong but not brittle. They soften at 180 °C and exhibit a high resistance to oxidation.

Table 2. The properties of polycarbonates and copolycarbonates based on 1,3-bis(4′-hydroxyphenyl)adamantane and bisphenol A.[63,64]

Property	Bisphenol A	1,3-bis(4′-hydroxyphenyl)adamantane	Bisphenol A: 1,3-bis(4′-hydroxyphenyl) adamantane = 1 : 1
Glass point, °C (DTA)	150	225—250	211—212
M.p., °C	220—230	stable up to 300	—
τ_0, °C	—	285	250
η_{in} (in methylene chloride)	0.59	0.69	0.76
n_D^{20}	1.585	1.578—1.582	1.582—1.586
Shore hardness	80±2	83±2	80±1
σ_t, MPa	85.5	58	91
ϵ_{rel}, %	80	8	19
E_t, MPa	1650	868	800
Density, g cm^{-3}	1.199	1.148	1.167

Bisphenols derived from adamantane have been used in the synthesis of polycarbonates and copolycarbonates. 1,3-Bis-(4′-hydroxyphenyl)adamantane is treated with phosgene in solution in methylene chloride in the presence of pyridine at 25—30 °C.[63] The copolycarbonate derived from 1,3-bis(4′-hydroxyphenyl)adamantane and 2,2-bis(4′-hydroxyphenyl)-propane (bisphenol A), taken in equimolar proportions, is obtained under analogous conditions[64]. Table 2 presents

certain properties of adamantane-containing co- and polycarbonates and compares them with a commercial polycarbonate—Lexan.

Bisphenols containing the adamantane nucleus in the form of a cardo-group have also been proposed for the synthesis of polycarbonates[65]. Depending on the method of preparation (low-temperature or interfacial polycondensation), these polycarbonates have crystalline or amorphous structures. The presence of adamantyl cardo-groups in the polycarbonates leads to an appreciable increase of their heat resistance and thermal stability. Depending on the structure of the bisphenol, the softening temperature is 240–310 °C and the temperature of the onset of decomposition is 300–350 °C.

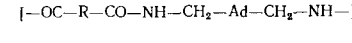
IV. ADAMANTANE-CONTAINING POLYAMIDES

Polyamides are some of the first polymers for which the effectiveness of the introduction of adamantane nuclei into polymer chains has been demonstrated. Adamantane-containing polyamides, obtained in the melt, like nylon-6,6, from a salt of 1,3-diaminoadamantane and sebacic acid[66] or a salt of adamantanedicarboxylic acid and 1,4-bis(aminomethyl)-cyclohexane[67], have a low molecular weight.

The conditions for the synthesis of the polyamides from the chloride of adamantane-1,3-dicarboxylic acid by emulsion and interfacial polycondensation have been studied in detail[67–69].

In the first case a high-molecular-weight polyamide (η_{ln} = 1.45) can be obtained in a high yield by carrying out the process in the presence of a small excess of the acid chloride at 10–30 °C and for an overall concentration of the reactants of 0.33 M. The reaction is performed by pouring a solution of the acid chloride in tetrahydrofuran (THF) into an aqueous solution of the diamine. Sodium carbonate is used as the HCl acceptor. In the interfacial polycondensation a solution of the acid chloride in an aromatic or chlorinated hydrocarbon is added with stirring to an aqueous solution of the diamine. Pyridine, triethylamine, and NaOH can also serve as the HCl acceptors.

High-molecular-weight polyamides with $\eta_{ln} \leq 5.0$ and having the general formula[70]



where R is a residue of an aromatic or aliphatic dicarboxylic acid, have been obtained by the solid-phase polycondensation of a salt of a mixed diamine—1,3-bis(aminomethyl)adamantane—with a dicarboxylic acid. The properties of the polyamides obtained are presented in Table 3.

Among adamantane-containing polyamides, poly(*m*-phenyleneadamantylene-1,3-dicarboxamide)—the product of the condensation of *m*-phenylenediamine with the chloride of adamantane-1,3-dicarboxylic acid—is of greatest interest:

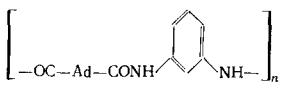
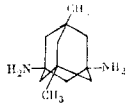
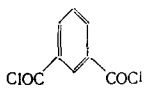
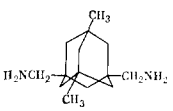
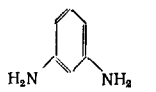
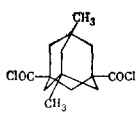
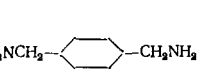
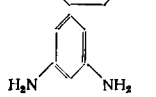


Table 3. The properties of adamantane-containing polyamides.

Dicarboxylic acid or its chloride	Diamine	η_{ln}^{+}	M.p., °C	Characteristics of polymer**	References
$HOOC(CH_2)_6COOH$	H_2N—Ad—NH_2	—	153	—	[66]
ClOC—Ad—COCl	H_2N—Ad—NH_2	0.11	—	—	[66]
ClOC—Ad—COCl		0.12	320	—	[67]
		0.82	240	transparent, vitreous	[70]
ClOC—Ad—COCl	$H_2N(CH_2)_6NH_2$	1.14	316	—	[69]
ditto	ditto	1.79	197	d = 1.16; σ_t = 50; ϵ_e = 3; σ_f = 327.5; water absorption = 0.34%	[69]
ClOC—Ad—COCl		1.45	294	d = 1.256; σ_t = 117; E_t = 586; ϵ_e = 13; water absorption = 1.52%	[49, 69]
	$H_2N(CH_2)_6NH_2$	1.46***	210***	σ_f = 110; E_f = 4280	[49, 67]
ditto	H_2NCH_2——CH_2NH_2	0.21	—	brittle	[67]
»		0.75	320	σ_t = 65.5; ϵ_e = 16	[49, 67]

* For polyamides Nos. 5–7, in concentrated sulphuric acid; for the remaining polymers, in *m*-cresol.

** Notation: E_t = tensile modulus (MPa); for the remaining notation, see the footnotes to Tables 1 and 4.

*** Molecular weight (3–4) × 10^4.

**** Glass point 145 °C.

Films and fibres can be obtained from it by appropriate methods. The properties of a polyamide film of this kind are presented in Table 4.[49] The polyamide softens at 294 °C and loses not more than 0.86% of its weight on being kept in air for 2 h at 325 °C.

Table 4. Properties of a poly-*m*-phenyleneadamantane-1,3-dicarboxamide film[49].

Property*	20° C	150° C	250° C
σ_f	153.8	—	—
E_f	4178	—	—
σ_t	117.2	75.8	34.5
ϵ_e	13	11	6
H_R	112	—	—

* Notation: σ_f = flexural strength (MPa); E_f = flexural modulus (MPa); σ_t = tensile strength (MPa); ε_e = elongation at break (%); H_R = Rockwell hardness.

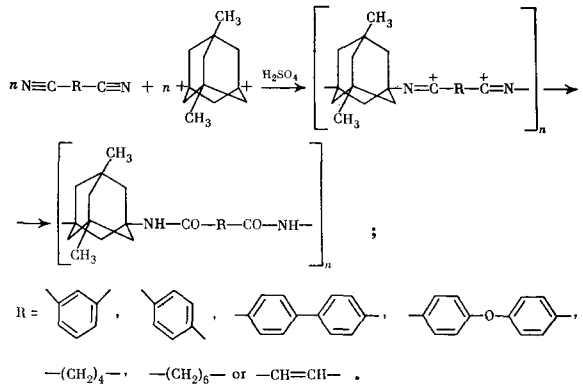
A fibre can be obtained from a solution of this polyamide in DMF by the wet moulding method[71]. An interesting feature of poly(*m*-phenyleneadamantylene-1,3-dicarboxamide) is that both the polyamide itself and the fibre obtained from it are amorphous and, in contrast to many polymers, the fibre does not crystallise on being kept at temperatures in the range between the glass and yield points. A special technique was therefore developed for drawing the moulded fibre in contact with a hot plate which makes it possible to follow the morphological changes occurring in the fibre during such treatment over a narrow temperature range[72]. The fibre has been drawn at 325 °C with a drawing factor of 6:1 and at a drawing rate of 220000% min^{-1}. The properties of the drawn fibre are presented in Table 5.[73]

Table 5. The properties of fibre based on poly-*m*-phenyleneadamantylene-1,3-dicarboxamide.

Property	Fibre	
	moulded	drawn
[η] (conc. sulphuric acid)	1.5	—
Linear density (denier)	—	7.3
Strength, g $denier^{-1}$	0.62	4.0
Initial modulus, g $denier^{-1}$		51.4
ϵ_e, %	19.9	—
Elasticity, %	72.2	25.2

However, in this case too the crystallinity of the fibre is low. The fibre is crystallised when it is kept in DMF or dimethylacetamide vapour. The fibre which was extended beforehand crystallises under these conditions in the course of several seconds[74]. The polyamide fibre has a high thermal stability, retaining 50% of its initial strength on being kept at 250 °C for 100 h[71].

A method employing the ability of dihalogeno- or dihydroxyadamantanes to form carbonium ions in highly ionising medias such as concentrated sulphuric or polyphosphoric acid has also been proposed for the synthesis of adamantane-containing polyamides[75,76]. The second reagent is an aliphatic, aromatic, or alicyclic dinitrile. The concentration of sulphuric acid is of decisive importance in this reaction; if it is below 99%, then the rate of polymerisation is low and the oxidative decomposition of the reactants predominates. At an acid concentration above 118% the process becomes difficult to control and is accompanied by the decomposition of the polyamide formed. The mechanism of this reaction can be illustrated by the following scheme:



In sulphuric acid, the reaction is carried out in the temperature range between −10° and 20 °C and in polyphosphoric acid between 70° and 110 °C. Polyamides have been obtained by this method in almost quantitative yields with η_{ln} between 0.5 and 1.2 and glass points in excess of 300 °C.

V. ADAMANTANE-CONTAINING POLYURETHANES

Adamantane-containing polyurethanes can be obtained by the reaction of 1,3-adamantylene di-isocyanate[77] or 1,3-di-isocyanato-5,7-dimethyladamantane[78] with polyols, which are usually polyalkylene or polyoxyalkylene glycols, polyester glycols, castor oil, and sorbitol polyesters. The reactivity of adamantylene di-isocyanate is considerably lower than that of aromatic di-isocyanates (Table 6). In the synthesis of adamantane-containing oligoester-urethanes it is therefore necessary to employ catalysts—NEt_3 or dibutyltindilaurate[80].

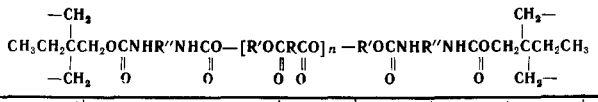
Table 6. The constants for the interaction* of di-isocyanates with poly(diethylene glycol adipate)[79].

Di-isocyanate	10^2k, litre mol^{-1} s^{-1}
2,4-Tolylene di-isocyanate	31.30
1,6-Hexamethylene di-isocyanate	5.26
1,3-Bis(isocyanatomethyl)adamantane	3.27
1,3-Adamantylene di-isocyanate	0.59

* k = reaction rate constant.

The hardening of liquid urethane rubbers with 1,1,1-tris-(hydroxymethyl)propane is fairly slow and the formation of a three-dimensional polyurethane network at 80 °C terminates after 10–12 h.[81] The properties of vulcanised polyurethanes are presented in Table 7. The increase in the chain lengths of oligomeric polyesterurethanes, based on tetramethylene glycol, when they interact with diamines[66] or with hydrazine hydrate[82] leads to the formation of light-resistant adamantane-containing polyurethane-ureas from which "Spandex" fibre is made. The films obtained from solutions of this polymer in DMF are transparent and have a low optical density and a high resistance to ultraviolet light (Table 8).

Table 7. The properties of adamantane-containing network polyurethanes* [81]



R	R′	R″	M_{av} (calc.)	10^3[Ad], mol g^{-1}	σ_t	ε_e, %	ε_0, %	TM2 hardness, rel. units	M.p., °C	$t_{o.d.}$
—$(CH_2)_4$—	—$(CH_2)_2$—O—$(CH_2)_2$—	—$(CH_2)_6$—	1280	0	9.3	450	1.5	0.56	—25÷—31	—
—$(CH_2)_4$—	ditto	—Ar—	1230	0	33.3	240	2.0	0.76	—15÷—22	270
—$(CH_2)_4$—	»	—Ad—	1420	1.41	37.1	225	1.5	0,80	20÷80	265
—$(CH_2)_4$—	»	—CH_2AdCH_2—	1480	1.35	23.5	380	2.5	0.60	2÷5	230
—Ad—	»	—$(CH_2)_6$—	1050	1.72	32.9	320	2.0	0,67	0÷8	240
—Ad—	»	—Ar—	1060	1.75	42.1	120	2.0	0.90	70÷74	270
—Ad—	»	—Ad—	1170	3.25	41.2	140	2.2	0.91	60÷66	270
—Ad—	—$(CH_2)_2O(CH_2)_2O(CH_2)_2$—	—$(CH_2)_6$—	1080	1.48	34.1	350	1.5	0.60	—10÷—16	—
—Ad—	ditto	—Ar—	1000	1.47	37,2	180	2.0	0.88	30÷36	—
—Ad—	»	—Ad—	1200	3.00	39.7	220	1.5	0.88	25÷30	250
Polyoxypropylene glycol		—Ad—	1550	1.29	17.2	478	2.5	1.00	—22÷30	220
—Ad—	—$(CH_2)_2$—O—$(CH_2)_2$—	—CH_2AdCH_2—	1230	3.12	24.5	285	3.0	0.73	38÷45	—

* Notation: Ar =  ; ε_0 = residual deformation at break; M_{av} = average molecular weight of the network polymer; $t_{o.d.}$ = temperature of onset of decomposition; for the significance of the remaining parameters, see the footnotes to Tables 1 and 4.

Table 8. Changes in the properties of linear polyurethanes on irradiation with ultraviolet light (in a AIPST-2-4-2 optical weather apparatus)[83]*.

Di-isocyanate	Before irradiation			After irradiation		
	σ_t	ϵ_e	D	σ_t	ϵ_e	D
1,3-Adamantylene di-isocyanate	3.3	187	0.1	2.2	122	0.14
Diphenylmethylene di-isocyanate	3.7	123	0,41	2.3	50	1.16
1,3-Bis(isocyanatomethyl) adamantane	3.1	346	0.1	2.2	245	0 14

* Notation: D = optical density (relative units); for the significance of the remaining notation, see the footnote to Table 4.

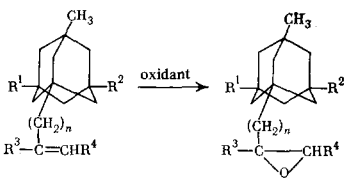
The replacement of 1,3-adamantylene di-isocyanate by 1,3-bis(isocyanatomethyl)adamantane makes it possible to obtain light-resistant polyurethanes with a higher elasticity[84]. An increase of light resistance is observed also for cross-linked polyurethanes. Thus polyurethane films obtained from poly(diethylene glycol adipate), 1,3-adamantylene di-isocyanate, and 1,1,1-tris(hydroxymethyl)propane turn yellow to a much lesser extent and lose 33% of the initial strength on irradiation with ultraviolet light, compared with films based on 2,4-tolylene di-isocyanate (72% loss of strength).[85] The rate of gas evolution from adamantane-containing polyurethanes under these conditions is lower by a factor of two, while the rate of absorption of oxygen is lower by a factor of 1.5 than for polyurethanes based on 1,6-hexamethylene di-isocyanate and 2,4-tolylene di-isocyanate.

Another advantage of adamantane-containing polyurethanes is their increased hydrolytic stability. This effect is particularly notable when the adamantylene group is attached to an ester group, i.e. for polyurethanes obtained from adamantane-containing oligoester-glycols[85]. The films obtained from such a polyurethane do not change in the course of three months in 5% H_2SO_4 and NaOH solutions and swell only by 3%, while similar polyurethanes derived from aliphatic oligoester-glycols decompose after 20–25 days.

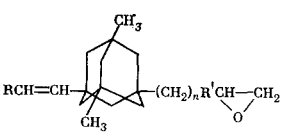
The products of the interaction of 1,3-adamantylene di-isocyanate with 1,3-diaminocyclohexane or 1,4-diaminobutane as well as butane-1,4-diol have been described[66]. In the first case the products are polyureas soluble in DMF and melting at 275 °C and in the second the product is a thermoplastic film-forming polyurethane.

VI. EPOXY-RESINS BASED ON ADAMANTANE DERIVATIVES

Adamantane-containing epoxides have been obtained by the oxidation of the corresponding alkenyladamantanes[86,87]:



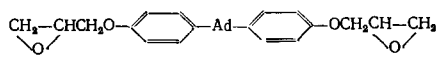
The oxidants are organic and inorganic peroxides, hydroperoxides, and hydrogen peroxide. The oxidation is carried out in the liquid phase in the temperature range from 5° to 50 °C in the presence of $Mo(CO)_6$. Epoxyadamantanes are obtained in yields up to 86% and are purified by distillation. Vinyl- and allyl-epoxyadamantanes having the general formula



can be obtained in this way. Polymerisation of these compounds in the presence of tri-isobutylaluminium and aluminium trisacetylacetonate yielded polyepoxides which are viscous liquids or solids and are likely to be useful as additives to lubricating oils and as components of adhesives. Polyepoxides with vinyl or allyl groups can be vulcanised, giving rise to rubber-like materials[86].

The reaction of adamantane-1,3-diol with the anhydride of cyclohexenecarboxylic acid led to the formation of a diester, which was converted into the bis-3,4-epoxycyclohexanecarboxylic acid ester of adamantane-1,3-diol by epoxidation with peracetic acid[88]. The product has a melting point of 31–32 °C and contains 19.8% of epoxy-groups.

The bisphenol derived from 5,7 dimethyladamantane[89], which reacts with epichlorohydrin in the presence of NaOH at 85–100 °C, is used as the starting compound for the synthesis of epoxy-resins. After isolation and washing free of salts, by the usual methods, the epoxy-resin

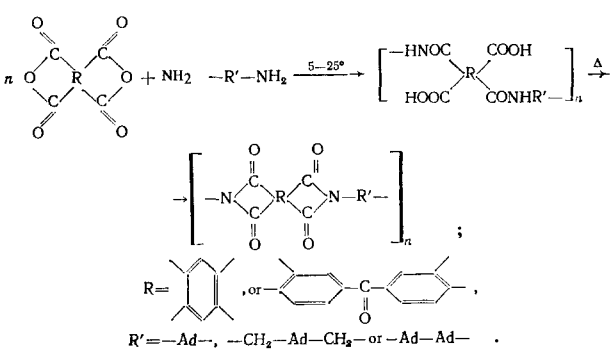


is a solid glass-like product of amber colour which melts at 47 °C.

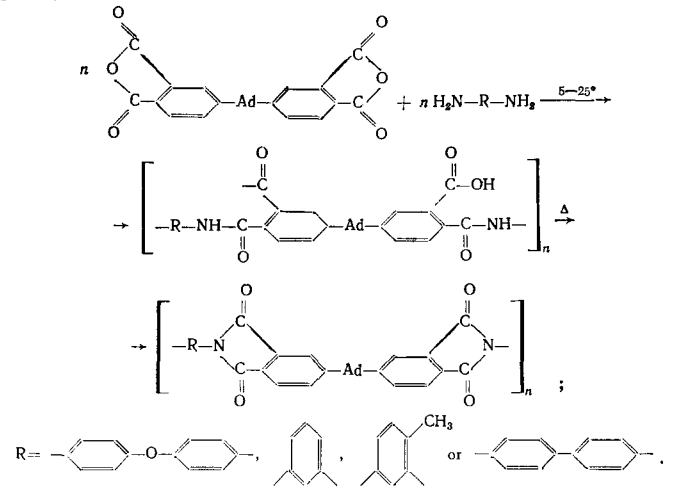
The hardening of epoxy-resins based on the bisphenols derived from adamantane, 1,1'-biadamantane, and isopropylidene on heating has been investigated[90,91]. The degree of hardening was inferred from the disappearance of the 415 cm^{-1} absorption band (due to the epoxy-group) in the infrared spectra and from determinations of the hardness of the specimens. Complete hardening was achieved after 13 h at 165 °C for the diglycidyl ether of the isopropylidenebisphenol, after 20 h at 200 °C for the diglycidyl ether of the bisphenol from adamantane, and after 88 h at 250 °C from the diglycidyl ether of the bisphenol from 1,1'-biadamantane. The hardened epoxy-resins derived from adamantane and 1,1'-biadamantane are superior as regards heat resistance and thermal stability to the polyepoxide with the isopropylidene groups. The softening temperatures of these resins are 250° and 220 °C compared with 180 °C for the polyepoxide based on the isopropylidenebisphenol, while the temperature of the onset of weight loss is 390° against 340 °C. In addition, they decompose at 400 °C leaving a larger amount of carbon residue than the corresponding polyepoxides without adamantane rings.

VII. CYCLOCHAIN POLYMERS OF ADAMANTANE

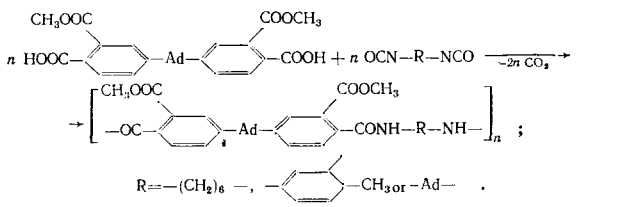
Among the cyclochain polymers with adamantane fragments in the main chain, polyimides have been most thoroughly investigated. They have been synthesised by a two-stage scheme. In the first stage a polyamidoacid is obtained by the reaction of diaminoadamantane with the dianhydride of an aromatic tetracarboxylic acid[92,93]:



The polyamidoacid is an intermediate in the reaction between an aromatic diamine and 1,3-bis(3',4'-dicarboxyphenyl)adamantane[94,95]:



In the second stage the polyamidoacid is subjected to cyclodehydration by heating it *in vacuo* at temperatures up to 300 °C. The reaction between the adamantane-containing dianhydride and the adamantane-containing diamine leads to low-molecular-weight polyamidoacids which are insoluble in organic solvents[92,96]. A similar result has been noted also in the synthesis of polyamidoesters by the reaction of the dimethyl ester of 1,3-bis(3',4'-dicarboxyphenyl)adamantane with di-isocyanate[97]:



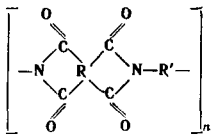
The basicity of adamantane-containing diamines is fairly high (pK_{a1} = 16.22–17.75) and that of 1,3-bis(aminoethyl)adamantane is at the level of aliphatic amines[98]. The formation of low-molecular-weight polyamidoacids is more likely to be explained by the low solubility and the reduced reactivity of the adamantane-containing dianhydride[99].

High-molecular-weight soluble adamantane-containing polyamidoacids with an intrinsic viscosity up to 4.8 dl g^{-1} are obtained when the above reactions are carried out in an aprotic solvent—inorganic salt system[100]. For example, in the presence of LiCl the rate constants for the formation of adamantane-containing polyamidoacids increase by a factor of 5–5.5.[99]

A distinctive feature of adamantane-containing polyimides is their high resistance to hydrolysis and the action of organic solvents and certain chemicals. A film made of the polyimide based on 1,3-bis(3',4'-dicarboxyphenyl)adamantane and di(4-aminophenyl)ether loses not more than 14% of its initial strength after a five day exposure to a 10% solution of NaOH and does not dissolve in concentrated H_2SO_4; on the other hand, the polyimide film based on pyromellitic dianhydride decomposes under analogous conditions[95].

A similar effect is also achieved when 1,3-bis(aminoethyl)-adamantane is used[101]. The introduction of 20% of this diamine instead of di(4-aminophenyl)ether in the synthesis of a polyimide based on pyromellitic dianhydride increases by a factor greater than 2 the hydrolytic stability of the polyimide film.

Table 9. The properties of adamantane-containing polyimides.



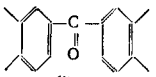
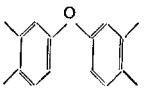
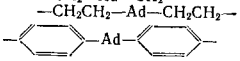
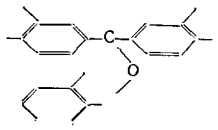
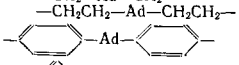
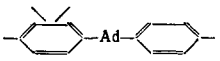
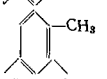
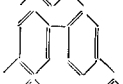
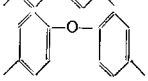
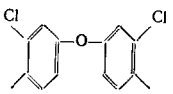
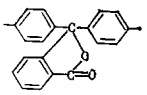
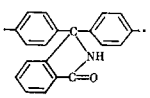
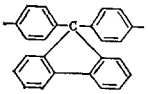
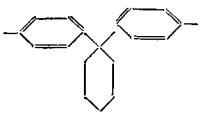
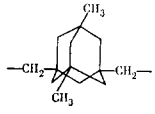
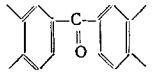
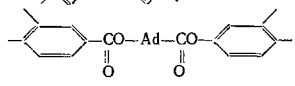
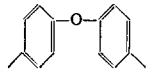
R	R'	η_{int}* (PAA)	M.p., °C	$t_{o.d.}$, °C	Characteristics of polymer**	References
	—Ad—	—	310	400	—	[93. 103]
ditto	—CH_2—Ad—CH_2—	—	210	390	—	[93. 103]
»	—Ad—Ad—	—	—	330	—	[93]
	—Ad—	—	240	380	—	[93. 103]
ditto	—CH_2—Ad—CH_2—	—	200	340	σ_t = 131.3	[93, 103]
»	—Ad—Ad—	—	—	330	—	[93]
	—Ad—	0.10	230	360	crystalline	[104. 108]
ditto	—CH_2—Ad—CH_2—	0.87	215	450	amorphous	[104, 108]
»	—CH_2CH_2—Ad—CH_2CH_2—	0.44	165	410	ditto	[104. 108]
»		0.78	305	440	»	[104 108]
	—Ad—	0.26	290	430	»	[104. 108]
ditto	—CH_2—Ad—CH_2—	0.83	260	425	amorphous	[104, 108]
»	—CH_2CH_2—Ad—CH_2CH_2—	0.34	215	415	ditto	[104, 108]
»		0.89	350	430	»	[104, 108]
		1.72	—	380	σ_t = 105.8; ϵ_e = 5–7; d = 1.48	[94, 95, 100]
ditto		4.80	—	—	—	[100]
»		1.59	—	380	σ_t = 90.2; ϵ_e = 3–6; d = 1.42	[94, 95, 100]
»		3.30	—	380	σ_t = 112.7; ϵ_e = 5–8; d = 1.44	[94, 95, 100]
»		2.20	—	345	σ_t = 106.8; ϵ_e = 5–7; d = 1.46	[94, 95, 100]
»		0.19	—	—	—	[100]
»		1.02	—	420	—	[102]
»		0.96	—	415	—	[102]
ditto		1 26	—	425	—	[102]
»		0.68	—	410	—	[102]

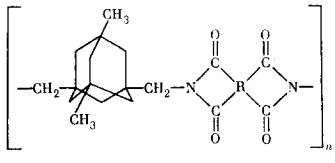
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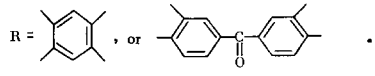
R	R′	η_{int}* (PAA)	$t_{o.d.}$, °C	M.p., °C	Characteristics of polymer**	References
		—	—	370	—	[105, 106]
	ditto	—	—	370	—	[105, 106]
		—	235	390	—	[107]

* In *N*-methyl-2-pyrrolidinone at 25 °C; PAA = polyamidoacid.
** For the designations and dimensions of the parameters, see the footnotes to Tables 1 and 4.

A whole series of soluble adamantane-containing polyimides with a high resistance to hydrolysis and an increased resistance to thermal oxidation have been obtained from cardo-diamines and cardo-dianhydrides[102-104]. They were synthesised in a single stage by heating the reactants in nitrobenzene to 210 °C. The polyimides soften on heating and can be worked by pressing or by casting from solution.

The polyimides obtained from the dianhydrides of aromatic tetracarboxylic acids and 1,3-bis(aminomethyl)-5,7-dimethyladamantane have an interesting property[105,106]:

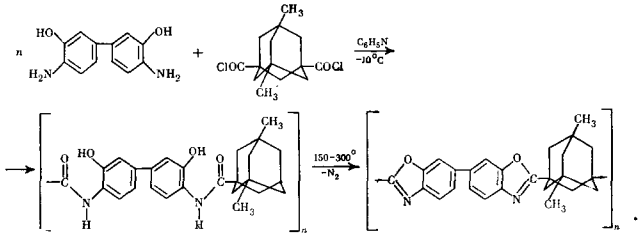




While their thermal stability is not inferior to that of aromatic polyimides, they are colourless—in contrast to the former polymers they do not have a characteristic yellow colour. Compared with similar polyimides based on 1,3-diaminoadamantane, they have a higher molecular weight. The properties of the polyimides synthesised are presented in Table 9.

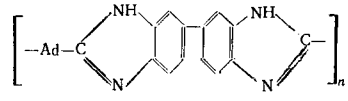
Heat-resistant polyester imides are obtained by the reaction of aromatic diamines with 1,3-adamantylenebistrimellitic dianhydride[107]. The polyimidoacid obtained in the first stage (viscosity 5.5 S) is converted into the imido-form at 300 °C for 16 h. The resulting polyester-imide film does not decompose on heating to 390 °C and has a glass point of 235 °C.

Adamantane-containing polybenzoxazoles obtained by low-temperature polycondensation from the chloride of 5,7-dimethyladamantane-1,3-dicarboxylic acid and 3,3′-dihydroxybenzidine have unusual properties[109]:



The prepolymer obtained in the first stage with η_{ln} = 1.13 gives rise to a colourless film soluble in water on pressing at specified temperatures. Thermal cyclisation of the film with a stepwise increase of temperature from 150° to 350 °C yielded a colourless polybenzoxazole soluble in water. The film has σ_t = 1.2 MPa and E_e = 210 MPa, losing ~ 10% of its weight on heating to 500 °C.

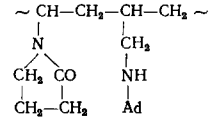
The synthesis of a polybenzimidazole from the diphenyl ester of adamantanedicarboxylic acid and 3,3′-diaminobenzidine has been described[110]:



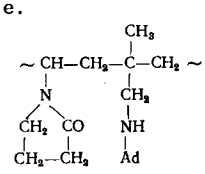
The polymer has a low molecular weight (η_{ln} = 0.19) and is soluble in DMF and dimethyl sulphoxide (DMSO), but its thermal stability is lower than that of aromatic polybenzimidazoles: it begins to decompose in nitrogen at 540 °C.

VIII. BIOLOGICALLY ACTIVE ADAMANTANE-CONTAINING POLYMERS

Progress in the chemistry of adamantane is to a large extent associated with the biological activity of some of its functional derivatives[6,21]. However, only a few studies have been made on the polymeric adamantane derivatives used in medicine. The copolymers of *N*-vinylpyrrolidinone and *N*-allylaminoadamantane[111]

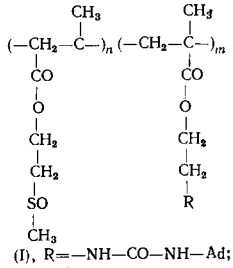


as well as the reduced products of the interaction of 1-aminoadamantane and the copolymer of *N*-vinylpyrrolidinone and crotonaldehyde[111], i.e.



have been proposed as potential antiviral agents. Water-soluble 2-(methylsulphinyl)ethyl methacrylate–2-*N*-(1′-adamantyl)ureidoethyl methacrylate (I) and the quarternary

ammonium salts of *N*-(1-adamantyl)chloroacetamide–2-dimethylaminoethyl methacrylate (II) copolymers have been described in another study[112]:

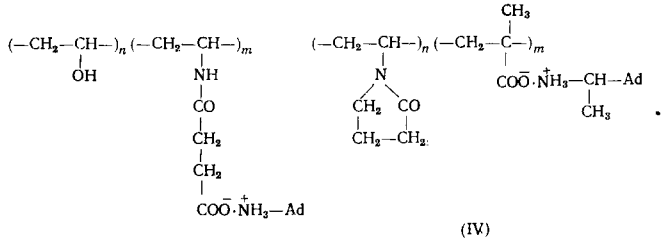


(I), R=—NH—CO—NH—Ad;

(II), R=—$\overset{+}{N}(CH_3)_2$—CH_2CONH—Ad .

It was found that only copolymer (II), containing ammonium groups, exhibits an antiviral activity.

Polymeric complexes of the salt type, obtained by treating with 1-aminoadamantane (III) and 1-(2′-aminoethyl)adamantane (IV) the copolymers of poly(vinyl alcohol) and *N*-vinylpyrrolidinone with *N*-vinylamidosuccinic and crotonic acids, have been studied in greater detail[113,114]:



(IV)

The study of the polymeric products showed that they are less toxic than the hydrochlorides of amino-derivatives of adamantane and that their prophylactic effect lasts five times longer. Two medicinal preparations with prolonged antiviral activity have been developed on their basis.

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Analysis of published data permits the definite conclusion that the introduction of the polyhedral adamantane molecule into polymers significantly improves some of their properties. The vast majority of adamantane-containing polymers are heat-resistant and soften at high temperatures. An important feature of these polymers is their high resistance to oxidation and hydrolysis and to the action of light and solvents. The properties of adamantane-containing polymers are superior to those of familiar industrial polymers and can find applications in various branches of technology.

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