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SYNTHESIS AND INVESTIGATION OF CROSSLINKED POLYMERS BASED ON ALIPHATIC BISMALEIMIDES AND CARDIC DIAMINES*

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Bismaleimides have been synthesized by reacting hexa-, octa- and decamethylenediamines with maleic anhydride. Crosslinked polyaminoimides were obtained by copolymerizing these bismaleimides with cardic diamines (anilinefluorene and anilinephthalein) and also with 4,4'-diaminodiphenylmethane and dodecamethylenediamine at various molar ratios. The strength, thermal and relaxational characteristics of the polymers were determined.

MUCH attention has been paid recently to the preparation of thermosetting polyimides from monomers or oligomers containing reactive furanyl [1], epoxide [2], acetylenic [3], ethylenic [4] and maleimide groups [5].

The interest in such polyimides arises from the fact that they form a three dimensional polymer network without evolution of any side products, which complicate the production of articles from linear aromatic polyimides obtained by imidization of polyamidoacids, and which impair their properties.

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The present paper describes an investigation of the properties of crosslinked polymers based on aliphatic bismaleimides and cardic diamines. The choice of these compounds for production of heat reactive polyimides arises from the fact that bismaleimides of aliphatic diamines have comparatively low melting points, enabling a crosslinked network to form in the melt at comparatively low temperatures. On the other hand the good solubility of linear polyamides and polyimides of high molecular weight derived from cardic diamines led us to expect good compatibility of such diamines with bismaleimides, because of the presence of the cardic groups, which should have a favourable effect on the strength properties of the final polymers.

Starting materials. Aliphatic bismaleimides of the general formula



(n=6, 8 and 10) were obtained by the one stage method, by reacting maleic anhydride with aliphatic diamines in the molar ratio of $5\cdot 5:1$ in acetic acid.

Hexamethylenediamine (11.6 g) was dissolved in 50 ml of glacial acetic acid in a four necked flask, provided with a thermometer, mechanical stirrer and reflux condenser. A solution of 58 g of maleic anhydride in 100 ml of acetic acid was then added. The reaction was carried out at 118-120°C for 8 hr. The reaction product was separated by precipitation in 1200 ml of water, filtered off, washed with water and dried, at first in air and then *in vacuo*, at 60°C. The products were purified by treatment with sodium bicarbonate solution, followed by high vacuum sublimation $((5-6) \times 10^{-3} \text{ torr})$. The final melting points of the bismaleimides with n=6, 8 and 10 were 139.5-141.5, 119.5-121.5 and 113.5-115°C respectively, in agreement with the literature [6].

The structure of the bismaleimides was confirmed by elementary analysis and IR spectroscopy.

The cardic diamines were purified by conventional methods and had melting points in agreement with the literature: 9,9-bis-(4'-aminophenyl)fluorene m.p. $234-235^{\circ}$ (sublimation at ~ 10^{-2} torr); 3,3-bis-(4'-aminophenyl)phthalide, m.p. $204\cdot0-204\cdot5^{\circ}$ C (recrystallization from ethanol).

The cardic diamines and aliphatic bismaleimides were reacted together in tubes sealed off in air, which were placed in a metal block previously heated to the desired temperature. After having been held at the fixed temperature for a certain time, the tubes were cooled, then opened and the polymers in the form of transparent continuous solid bodies, varying in colour from light yellow (homopolymers) to dark red (copolymers) were removed.

The yield of crosslinked polymer was determined from the quantity of insoluble fraction remaining after extraction of the ground polymers in a Soxhlet apparatus with acetone, which readily dissolves both the unreacted bismaleimides and the cardic diamines.

The mechanical and relaxational properties were determined with specimens cut from the unextracted polymer samples.

Reaction of the aliphatic bismaleimides with the cardic diamines (anilinefluorene and anilinephthalein), purely thermally or in the presence of benzoyl peroxide, yielded crosslinked polyamides, in which the quantity of insoluble fraction calculated on the total quantity of starting materials, increased from

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56-58% (1:1 copolymer) to 95-96% (homopolymer) as the diamine concentration was reduced (Table 1).

It is seen from the quantity of insoluble residue calculated with respect to the quantity of the bismaleimide, that at all ratios of the starting materials the yield of insoluble, crosslinked polymer is greater than the original quantity of bismaleimide. This indicates that together with homopolymerization of the bismaleimide or oligoimide, with formation of a crosslinked polymer, migrational copolymerization of the bismaleimide with the diamine also occurs.

Investigation of the effect of reaction time at 225° C on the yield of crosslinked polymer, showed that in copolymerization of N,N'-hexamethylenebismaleimide with anilinefluorene in equimolar proportions, the amount of insoluble fraction reaches 57% in 1 hr and then remains constant. It was shown that the reaction goes to approximately the same degree over the range of temperatures from 200 to 250°C (Table 1).

TABLE 1. YIELD* OF CROSSLINKED POLYMERS OBTAINED IN HOMOPOLYMERIZATION
of N,N'-hexamethylenebismaleimide and in copolymerization of the latter
WITH 9,9-BIS-(4'-AMINOPHENYL)FLUORENE

Molar ratio of N,N'-hexamethyl- enebismaleimide : 9,9-bis-	Insoluble fraction (% [†]) obtained at the tem- peratures			
(4-aminophenyl)fluorene	200°	225°	250°	
1:1.0	58/131	56/130	56/127	
1:1.0‡	63/144	63/143	64/146	
1:0.8	68/137	64/131	62/126	
1:0.8‡	83/167	80/161	89/149	
1:0.5	87/139	77/129	81/131	
1:0.5 [‡]	88/145	94/155	95/156	
1:0.2	89/104	95/111	96/112	
1:0.2‡	89/105	96/113	96/113	
1:0.1	95/106	98/108	97/109	
• 1:0·1‡	90/102	95/109	94/108	
1:0	96	96	96	
1:0‡	96	96	96	

(Reaction time 3 hr)

* The yield of crosslinked polymer was taken as the residue after extraction with acetone for 20 hr.

[†] The numerator is the percentage of the total weight of starting materials and the denominator, of the weight of maleimide.

[‡] In the presence of benzyol peroxide.

It seems, however, that it is preferable to carry out the reaction at 225° , because at 200° the diamine, when its quantity is high in relation to the bismaleimide, remains partially undissolved in the imide and obviously does not take part in copolymerization, while at 250° a very brittle polymer is formed.

When a bismaleimide is reacted with a diamine in the presence of benzoyl peroxide the quantity of insoluble product is a little higher than in purely thermal polymerization (Table 1), possibly because of a higher contribution by homopolymerization through the double bonds, resulting in formation of a network with a higher frequency of crosslinking. The greater brittleness of the solid block samples of the polymers (the most brittle polymers are obtained by homopolymerization of the bismaleimides) provides indirect evidence of this. As the mole fraction of the diamine is increased the brittleness of the end product decreases and the polymers easily undergo mechanical testing.

On the basis of these results the other polyaminoimides derived from N,N'-octaand N,N'-decamethylenebismaleimide with anilinefluorene and anilinephthalein, and from N,N'-hexamethylenebismaleimide with anilinephthalein in various ratios, were obtained purely thermally at 225° , whereby polymers containing 57-98% of insoluble fraction were obtained.

The thermal stability of the homo- and copolymers was investigated by the rising temperature TGA method in air (rate of heating 5 deg/min).

Bismaleimide	Cardic diamine	Molar ratio of bismale- imide : : diamine	Elasticity modulus in compres- sion, $E \times 10^{-4}$, kg/cm ²	Compres- sive strength, kg/cm ³
N,N'-Hexamethylenebis- maleimide	Anilinefluorene	1.0:0.5	3.5	2000
Ditto	,,	$1.0:0.5^{++}$	2.6	1900
3 9	,,	1.0:0.2	2.2	2000
33	Anilinephthalein	1.0:0.5	$3 \cdot 2$	2000
33	,,	$1.0:0.2^{+}$	$2 \cdot 5$	2300
N,N'-Octamethylenebismale- imide	Anilinefluorene	1.0:0.5	$2 \cdot 8$	1600
Ditto	Anilinephthalein	1.0:0.5	$2 \cdot 2$	1700
33	,,	$1.0:0.2^{+}$	$2 \cdot 0$	2000
N,N'-Hexamethylenebismale- imide	None		1.8	1800
N,N'-Octamethylenebismale- imide	None	-	1.5	1600

TABLE 2. STRENGTH AND ELASTICITY MODULUS IN COMPRESSION OF CROSSLINKED POLYMERS BASED ON ALIPHATIC BISMALEIMIDES AND CABDIC DIAMINES*

• Tests carried out with monolithic specimens measuring $2 \times 2 \times 4$ mm in a Dubov-Regel' apparatus at a rate of deformation of 1.87×10^{-1} mm/min.

* Reaction carried out in the presence of benzyol peroxide (1% on weight of bismaleimide).

It is seen from Fig. 1, which shows the TGA curves of four of the polymers as examples, that the highest temperatures of the onset of loss in weight ($\sim 400^{\circ}$ C) are found for the homopolymers of the aliphatic bismaleimides, which can be explained by a higher frequency of crosslinking in these polymers. Introduction of a cardic diamine such as anilinefluorene into the composition of the copolymer, although it lowers the initial temperature of loss in weight it makes the decomposition less rapid and raises the temperature of 100% weight loss. The inflexion in the TGA curve of the copolymer of the bismaleimide and anilinephthalein (molar ratio 1:1) can be explained by the effect of decomposition of lactone groups.



FIG. 1. TGA curves of polyhexamethylenebismaleimide (1) and of copolymers of N,N'-hexamethylenebismaleimide with anilinefluorene (2, 3) and anilinephthalein (4); molar ratio of bismaleimide : diamine = 1 : 1 (2) and 1 : 0.50 (3 and 4). Specimens heated in air at 5 deg/min.

FIG. 2. Curves delimiting the regions of stress resistance of polyhexamethylenebismaleimide obtained by thermal polymerization at 225°C (1) and of copolymers of N,N'-hexamethylenebismaleimide (2 and 3). The copolymers were prepared by thermal polymerization at 225°C and molar ratios of bismaleimide : diamine of 1 : 0.35 (2) and 1 : 0.50 (3); polymerization time 3 hr.

We studied the effect of the structure of the crosslinked polymer network on the strength characteristics of the original solid block specimens (Table 2). The mechanical and relaxational properties were investigated in the case of copolymers in which the content of crosslinked polymer was fairly high ($\geq 80\%$). Obviously only in that case is it possible to consider that the molar composition of the copolymers is close to the ratio of the compounds taken for reaction, and therefore the results obtained with the unextracted, block specimens can correlate with the chemical structure and composition of a particular copolymer. This situation is obtained fairly satisfactorily at ratios of the bismaleimides to diamines of 1.0:0.50, 1.0:0.35 and 1.0:0.20.

It is seen from Table 2 that the crosslinked polymers have fairly high compressive strength, reaching $2000-2500 \text{ kg/cm}^2$. It is interesting to note that when aromatic, cardic diamine units are introduced into crosslinked polymers based on aliphatic bismaleimides, both the compressive strength and the elasticity modulus are increased.

It is known that formation of a network can either increase or reduce the elasticity modulus. In our case, despite the higher crosslinking density of a homopolymer it has a lower elasticity modulus than when there is a greater distance between branch points as a result of introduction of anilinefluorene or anilinephthalein. The fact that increase in crosslinking density brings about a reduction in the modulus is conformed by the reduction in the elasticity modulus that is seen on passing from copolymers of N,N'-hexamethylene- and N,N'-octamethylenebismaleimide with anilinefluorene or anilinephthalein, obtained by thermal polymerization, to the corresponding copolymers prepared in the presence of benzyol peroxide (Table 2), which evidently directs the reaction in favour of homopolymerization of the bismaleimide.



FIG. 3. Curves delimiting the region of stress resistance of copolymers of N,N'-hexamethylenebismaleimide with anilinefluorene (a) and 4,4'-diaminodiphenylmethane (b). The copolymers were prepared at 225°C for 3 hr; molar ratio of bismaleimide : diamine=1:0.20.

Investigation of the softening points of the crosslinked copolymers by the thermomechanical method, did not reveal any effect of the chemical structure of the copolymers on the temperature at which deformation begins. All the polymers (the homo- and copolymers), with different numbers of methylene groups between the imide rings, begin to deform at about 400°C.

In order to obtain a more detailed analysis of the effect of the chemical composition of the three dimensional network on softening point, we studied the relaxation properties of the cardic diamine homo- and copolybismaleimides over a wide ringe of temperatures, strains and stresses. For this purpose the method described in reference [7] was used, involving nonisothermal stress relaxation in uniaxial compression, at a rate of rise in temperature of 4 deg/min. The dimensions of the specimens were $3 \times 3 \times 4$ mm.

It is seen from Fig. 2 that for the crosslinked homopolymer from N,N'-hexamethylenebismaleimide the curve defining the limit of the region of stress resistance is approximately vertical and lies in the region of very high temperatures. This is obviously attributable to the very high network density, when rapid acceleration of relaxation processes and loss of durability is caused by thermal breakdown of the crosslinked polymer, which, as already mentioned, is shown by the TGA results to begin at about 400°C.

The nature of the relaxational processes changes radically when the cardic diamine, anilinefluorene, unit is introduced into the network. The curves of nonisothermal stress relaxation in a copolymer containing a small quantity of that diamine (molar ratio of bismaleimide : anilinefluorene=1:0·2) contain two maxima, one in the region of comparatively low temperatures and high stresses, and the second in the region of high temperatures and comparatively low stresses (Fig. 3a). As the proportion of diamine units in the copolymer is increased from 0·2 to 0·5 mole per mole of bismaleimide the temperatures of the first maxima fall slightly (Fig. 2, curves 2 and 3), while the second maxima degenerate to a fairly long plateau. This behaviour of the crosslinked system can be explained by the fact that inclusion of the diamine units in the network results in formation of linear polyaminoimide fragments, i.e. to "dilution" of the network



Similar results were obtained when anilinefluorene was replaced by the other cardic diamine anilinephthalein.

When 4,4'-diaminodiphenylmethane is used instead of anilinefluorene, i.e. when the cardic fluorene grouping in the diamine is replaced by a methylene bridging group, the curve delimiting the region of stress resistance becomes sloped, and the second maximum that appears in the curves of the anilinefluorene copolymers and the plateau region, disappear (Fig. 3b).

It could be thought that this difference is due to steric hindrance to formation of the network when cardic, aromatic diamines are used, resulting in looser packing of the chains in the monolithic polymer specimen.

Table 3. Working data and the molar packing coefficients for the crosslinked polymer system based on N,N'-hexamethylenebismaleimide and anilinefluorene

Molar ratio of bis- maleimide : aniline- fluorene	Average MW of repeating unit	Molar van-der- Waals volume, cm ³ /mole	Density, g/cm³	Packing coef- ficient K
1:0	276.0	233.0	1.313	0.667
1.0:0.20	$345 \cdot 6$	$299 \cdot 4$	1.300	1.678
1.0:0.35	397.8	349.1	1.273	0.673
1.0:0.50	4 50·0	399 ·0	1.277	0.682
1.0:0.50*	375.0	329.7	1.270	0.672

• 4,4'-Diaminodiphenylmethane was used as the diamine.

Our calculations [8, 9] showed, however, that the coefficients of molecular packing when cardic diamines are used, are virtually the same as for N,N'-hexamethylenebismaleimide homopolymer and its copolymer with 4,4'-diaminodiphenylmethane (Table 3). It is evident that the cause of the difference must therefore be the greater chain flexibility of the copolymer of hexamethylenebismaleimide with 4,4'-diaminodiphenylmethane.

When N,N'-hexamethylenebismaleimide is replaced by N,N'-octamethylenebismaleimide the nature of the region of stress resistance does not change, but naturally there is a small reduction in the temperature boundary of the region. When the cardic diamine is replaced by 1,12-dodecamethylenediamine in reaction with N,N'-hexamethylenebismaleimide, the softening point of the polymer falls sharply, and for non-isothermal stress relaxation at an initial temperature of 20° C no maximum appears in the relaxation curves.

Thus the above crosslinked copolymers from bismaleimides of aliphatic and cardic diamines have high strength characteristics and a number of other specific properties.

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RELAXATIONAL PROPERTIES OF PLASTICIZED POLYAMIDE-12*

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The dielectric relaxation characteristics of polyamide-12 (polydodecalactam), plasticized by sulphonamides of the type $\text{RSO}_2\text{NHC}_4\text{H}_9$ (where R is phenyl, β -naphthyl, 3-pyridyl or 8-quinolyl), were studied over a wide range of temperatures and frequencies (-100°C to +100°C and 0.5-200 kHz). The glass temperature and relaxation time were determined, and the free energy, enthalpy and entropy of orientational dipole polarization of the systems were calculated. It is shown that the decrease in all these characteristics as the sulphonamide concentration is increased, indicates increase in the mobility of the structural elements of the system, and that heterocyclic and bicyclic sulphonamides give an improved plasticizing effect.

POLYAMIDE-12 (PA-12) which is one of the more promising polymers for the most widely differing branches of industry, provides a combination of high hardness and impact resistance with low density and good electrical insulating these being maintained under conditions of high humidity [1]. The plasticization of PA-12, which is done mainly for the purpose of improving the technological properties of the polymer, has received little study [2]. The effect of the structure of the plasticizer on the properties of PA-12 has not been described.

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