

Synthesis and Physico-Mechanical Properties of Aliphatic Polyesteramides

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Synopsis

Random polyesteramides with different chemical compositions and block polyesteramides have been prepared by a two-step polycondensation method from adipoyl dichloride, 1,10-decandiol, and 1,6-diaminohexane. A sample of alternating microstructure has been synthesized by melt polycondensation of 1,10-decandiol and preformed bisesteramides. The thermal and viscoelastic behavior has been investigated and related to the chemical composition and chain microstructure. The random copolymers exhibit one transition in the crystalline phase, whereas two transitions are shown by the block copolymers. The viscoelastic behavior suggests that in the amorphous component a partial microsegregation of phase occurs, generating an intermediate structure between a monophasic and a biphasic amorphous system.

INTRODUCTION

The polyesteramides were the object of extensive investigations in recent years. The main interest has been focused on ordered polyesteramides having a regular enchainment of ester and amide groups.¹⁻¹¹ These regularly alternating copolymers are semicrystalline materials of promising technological interest because of their good fiber forming properties. Some attention has also been devoted to block polyesteramides and especially to those designed to modify poly(ethylene terephthalate) or to obtain high tenacity filament yarns.¹²⁻¹⁵ Unsaturated polyesteramides, block and random, have also been prepared in order to improve the physical properties of unsaturated polyester resins after crosslinking with styrene.¹⁶⁻¹⁸ Finally, polyesteramides having no ordered structures have been reported mainly in the patent literature.¹⁹⁻²²

This work deals with the preparation and the characterization of aliphatic polyesteramides having a random distribution of —CONH— and —COO— groups along the chain and different composition or, alternatively, having different chain microstructure but equal chemical composition.

The thermal and viscoelastic properties of these copolymers were investigated and related to the chemical composition and functional group distribution law.

EXPERIMENTAL

Materials

Dry and alcohol-free chloroform was used in low temperature polycondensations. 1,10-Decandiol was distilled by vacuum sublimation, and 1,6-dimino-hexane was distilled from potassium hydroxide at reduced pressure. Technical grade titanium tetraisopropylate was purified by vacuum distillation before use. Adipoyl dichloride was prepared from adipic acid and thionyl chloride according to standard methods and distilled twice under vacuum before use.

Techniques

Infrared spectra of the copolymers were taken on films prepared by slow evaporation of formic acid solutions and recorded on a Perkin-Elmer 257 Spectrophotometer. NMR spectra were carried out by using a Varian EM-360 spectrometer operating at 60 MHz on formic acid solutions. The melting behavior was investigated by means of a Perkin-Elmer DSC-2 differential scanning calorimeter under nitrogen. The maximum of the DSC endotherm was taken as the melting point of the sample. The DSC temperature scale was calibrated against high purity standards. The apparent enthalpy of fusion ΔH_m was calculated from the area under the DSC traces using indium ($\Delta H_m = 28.5 \text{ J/g}$) as the standard.

The \bar{M}_n determinations by the vapor pressure osmometry method were performed in chloroform by Dr. Malissa and Reuter, Analytische Laboratorien (Germany).

The dynamic-mechanical behavior was analyzed using the Vibron Viscoelastometer of Toyo Instruments. The work frequency was 110 Hz. After a rapid cooling the dynamic spectrum was detected on heating the sample step by step in the temperature range $-100^\circ\text{C} \div \simeq T_m$ (melting temperature).

The complex modulus E^* and the loss term $\tan\delta$ were obtained and reported as a function of the temperature. Two experimental spectra were detected for each sample, and average E^* and $\tan\delta$ values were obtained when a satisfactory reproducibility was observed.

TYPICAL PREPARATIONS OF POLYESTERAMIDES

Alternating Polyesteramides

(i) Freshly distilled adipoyl chloride, 11.90 g (65.0 mmol), dissolved in 125 mL of chloroform was added dropwise, under stirring, to a 250-mL chloroform solution containing ethyl 6-aminocaproate, 20.3 g (128 mmol), and triethylamine, 12.93 g (128 mmol) for 40 min. The temperature was kept at $0-5^\circ\text{C}$. The solution was left at room temperature for an additional hour and then chloroform was distilled off until the volume was 150 mL. *N*-hexane (600 mL) was added and the obtained precipitate was collected on a glass filter and repeatedly washed with water. The crude product was twice crystallized from toluene and 26.31 g (yield 92%) of pure bis(*N*-carboethoxypentyl)adipamide, mp $113-114^\circ\text{C}$, were obtained.

(ii) Bis(*N*-carboethoxypentyl)adipamide, 4.22 g (9.9 mmol), 1,10-decandiol,

5.22 g (30.0 mmol), and titanium tetraisopropylate, 0.016 g (0.05 mmol) in isopropyl alcohol (0.2 mL), were placed under nitrogen in a glass vial equipped with a capillary tube for nitrogen inlet and a side arm for volatile products distillation. The mixture was heated at 200–210°C for 3 h under a nitrogen stream until the ethyl alcohol formed was distilled off through the side arm and collected in order to follow the reaction progress. Thereafter, the pressure was gradually reduced to 0.05 torr within 1 h while the excess of the diol, was distilled off too. Finally the mixture was heated for an additional hour at 250°C, yielding 4.84 g of polymer (95% yield).

Block Polyesteramides

(i) 1,10-Decandiol, 1.41 g (8.1 mmol), was added under nitrogen to adipoyl chloride, 1.90 g (10.4 mmol). The mixture was slowly heated up to 80°C under stirring and kept at this temperature for 1 h until the hydrogen chloride evolution ceased. Thereafter, more adipoyl chloride, 1.72 g (9.5 mmol), was added and the reaction was carried out for an additional 1 h. The reaction mixture was dissolved in 50 mL of chloroform, and the resulting solution was rapidly added under a vigorous stirring to a solution of 1,6-diaminohexane, 1.39 g (12.0 mmol) and sodium hydroxide, 0.96 g (24.0 mmol), in 150 mL of water. The precipitated polymer was collected on a glass filter, washed repeatedly with distilled water, and finally dried in a vacuum oven (0.1 torr) at 50°C for 48 h. Yield: 3.25 g (65%).

(ii) In a similar experiment 1.83 g (10.0 mmol) of adipoyl chloride and 1.43 g (8.2 mmol) of 1,10-decandiol were reacted. At the end of reaction, more adipoyl chloride (1.83 g, 10 mmol) was added, and the reaction was carried out for an additional 1 h. Most of unreacted adipoyl chloride was distilled at 0.01 torr and 80°C, and the residue was hydrolyzed with water. After many extractions with water, the product was dried in a vacuum oven (2.05 g, 88% yield based on the diol). The oligoester had $\bar{M}_n = 1520$ g/mol as determined by vapor pressure osmometry in chloroform and $T_m = 72^\circ\text{C}$, determined by DSC. The titration of the carboxyl end groups in benzene required 1.21 meq/g of potassium hydroxide (functionality equal to 1.84 end groups per macromolecule).

Random Polyesteramides

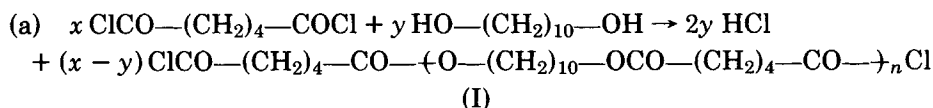
1,10-Decandiol, 1.74 g (10.0 mmol), was added under nitrogen to adipoyl chloride 3.66 g (20.0 mmol). The mixture was slowly heated up to 80°C under stirring, kept at this temperature for 1 h until the hydrogen chloride evolution ceased and finally dissolved in 50 mL of chloroform. The solution was rapidly poured under vigorous stirring into a blender containing a solution of 1,6-diaminohexane, 1.16 g (10.0 mmol), and sodium hydroxide, 0.80 g (20.0 mmol), in 125 mL of water. After 10 min, the stirring was discontinued, and the polymer was collected, repeatedly washed with distilled water, and finally dried at 50°C and 0.1 torr for 48 h (yield: 4.44 g, 87%).

RESULTS AND DISCUSSION

Synthesis and Characterization

The polyesteramides investigated in this work are reported in Table I. According to the distribution law of ester and amide groups along the chain, we can envisage the three fundamental classes of copolymers, i.e., random, block, and regularly alternating polyesteramides. Appropriate synthesis methods were employed to obtain these microstructures.

Copolymers of different chemical compositions having a disordered distribution of —CONH— and —COO— groups were prepared utilizing the scheme outlined below (Scheme 1) (preparation of polyesteramides of disordered chemical structure):



$n = 0, 1, 2, \dots$



First, (a) an excess of adipoyl dichloride was reacted in bulk at moderate temperatures ($<100^\circ\text{C}$) with 1,10-decandiol to give a mixture of oligomers of type I ($n = 1, 2, 3, \dots$), having functional COCl groups as chain ends, together with a variable amount of unreacted adipoyl dichloride (indicated in the scheme as compound I having $n = 0$).

This formation method of ester bonds for the synthesis of polymers was first proposed by Flory²³ and used by us for the synthesis of several aliphatic polyesters²⁴ and for the preparation of block polyamidoethers having polyamide and polyether blocks linked by ester groups.²⁵ The mixture formed in step (a) was dissolved in chloroform and polymerized with the stoichiometric amount of 1,6-diaminohexane either by solution or interfacial low temperature polycondensation. The yields obtained by the two methods are comparable; however, the viscosity values for copolymers prepared by the interfacial technique were

TABLE I
Aliphatic Polyesteramides of Different Chain Microstructure

Polymer	Structure	Molar fraction CONH ^a		η_{inh}^b (dL/g)	Yield (%)
		Calcd	Found		
PEA 1	random	0.91	0.81	1.03	65
PEA 2	random	0.75	0.69	1.70	73
PEA 3	random	0.66	0.58	0.94	86
PEA 4	random	0.50	0.43	0.94	87
PEA 5	random	0.33	0.27	0.61	88
PEA 6	block ^c	0.60	0.50	1.21	70
PEA 7	block ^c	0.70	0.57	0.91	65
PEA 8	alternating	0.50	0.51	0.68	95

^a Molar ratio CONH/(COO + CONH) as calculated from the reaction stoichiometry and as found by PMR spectroscopy and elemental analysis.

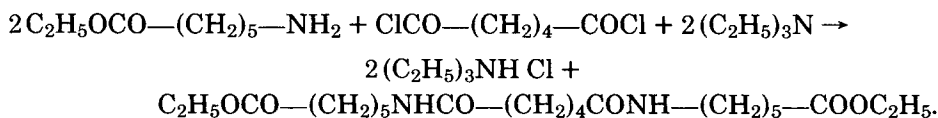
^b Inherent viscosity in *m*-cresol at 25°C, $c = 0.5 \text{ g/dL}$.

^c Number average molecular weights of the polyester blocks calculated from the stoichiometric ratio $q = y/x$ were of 800 and 1100 g/mol for PEA 6 and PEA 7, respectively.

always higher than those found for copolymers of nearly equal composition prepared by the solution technique. Both the average values of n (Scheme I), as well as the chemical composition of the polyesteramide, clearly depend on the x/y ratio. Polyesteramides of very high ester content could not be obtained by the method outlined in Scheme I because the fraction of oligomers (I) having hydroxyl end groups, unreactive in the subsequent step (b), is not negligible when the value of y approaches that of x . Therefore, attempts to obtain such copolymers yielded low-molecular-weight materials, as suggested also by the inherent viscosity which values decrease as the ester content from PEA 1 to PEA 5 increases (see Table I). The actual distribution of COO and CONH groups along the copolymers chain cannot be exactly described owing to the nonequilibrium character of both (a) and (b) reactions, apart from possible different reactivity of —COCl end groups attached to oligomers of different sizes. Considering the absence of an ordered structure, the copolymers prepared by this scheme, viz., PEA 1, PEA 2, PEA3, PEA 4, and PEA 5, will be referred as "random" polyesteramides.

In order to obtain blocklike polyesteramides, some modifications to Scheme 1 were necessary. First, in step (a) the stoichiometric ratio ($q = y/x$) was kept close to 1 to yield oligoesters (I) of moderate polymerization degree [$\bar{P} = (1 + q)/(1 - q) = 5\text{--}7$, by assuming the extent of reaction equal to 1].

These oligoesters, having both hydroxyl and acid chloride end groups, were subsequently reacted again with a large excess of adipoyl dichloride in order to obtain telechelic polyesters bearing only —COCl groups as chain ends. Finally, the telechelic polyesters and the unreacted adipoyl dichloride were dissolved in the appropriate solvent and chain extended with the diamine [step (b)]. Under separated experiment the telechelic polyester was isolated before the reaction with the diamine [step (b)] in order to check its formation, and the —COCl end groups were hydrolyzed to carboxyl groups. The found number average molecular weight, 1520 g/mol, was close to that calculated from the stoichiometric ratio q , 1440 g/mol, $\bar{M}_n = M_0\bar{P} = M_0(1 + q)/(1 - q)$. The analysis of carboxyl end groups yielded a value of 1.84 carboxyl groups per macromolecule. By varying the value of q in step (a) and the value of the excess of adipoyl chloride, it was possible to change in a concerted way the average sequence length of both polyester and polyamide blocks at a fixed copolymer composition. The two blocklike copolymers thus prepared, PEA 6 and PEA 7, have blocks of relatively small size and high values of viscosity (see Table I); therefore, their architecture is of the -(AB)-_n type. They have similar compositions near to 1:1 molar ratio of COO and CONH groups. For the synthesis of the alternating polyesteramide, the amide bonds were performed by a Shotten-Bauman condensation reaction between the adipoyl chloride and the ethylester of ϵ -aminocaproic acid in chloroform solution and in the presence of triethylamine as acid acceptor:



The diesters having performed amide groups were thereafter polymerized in the melt with 1,10-decandiol as indicated in Scheme 2 (preparation of a polyesteramide of alternating structure):

TABLE III
 Fractionation of Some Polyesteramides by Chloroform Extraction

Copolymer	PEA 3			PEA 6		
	Relative amount (%)	Composition ^a	η_{inh}^b (dL/g)	Relative amount (%)	Composition ^a	η_{inh}^b (dL/g)
Crude copolymer	100	0.58	0.94	100	0.50	1.21
Soluble fraction	25	0.35	0.42	20	0.32	1.01
Insoluble fraction	75	0.65	1.15	80	0.55	1.36

^a Molar ratio CONH/(CONH + COO).

^b Inherent viscosity in *m*-cresol at 25°C, *c* = 0.5 g/dL.

showing, however, an increased solubility in strongly polar solvents such as chloroform and *N,N*-dimethylacetamide. We have found that repeated chloroform extractions on some random and block copolymers yield 15–30% of a soluble fraction. These fractions showed an enrichment in ester groups and a decrease of the viscosities, and indicated a partial fractionation with respect to both composition and molecular weight. In Table III are reported, as an example, the results obtained for the PEA 3 and PEA 6 copolymers. However, it is important to remark that polyester homopolymer contamination was not even found in copolymers, the initial composition of which is richer in ester groups.

Physical Properties

The physical properties of the copolymers reported in Table I were analyzed using the differential scanning calorimetry and the dynamic-mechanical spectroscopy as experimental techniques. In Table IV the transition temperatures

TABLE IV
 Calorimetric Data of Aliphatic Polyesteramides

Polymer	Transition I		Transition II	
	ΔH_m (J/g)	T_I (K)	ΔH_m (J/g)	T_{II} (K)
PEA 1	a	—	53.6	521
	b	—	38.5	519
PEA 2	a	—	33.1	511
	b	—	15.9	503
PEA 3	a	—	22.2	515
	b	—	19.3	516
PEA 4	a	trace	trace	515
	b	—	—	—
PEA 5	a	16.7	—	—
	b	21.3	340	—
PEA 6	a	15.9	22.6	516
	b	—	19.3	515
PEA 7	a	20.1	28.5	521
	b	9.6	340	519
PEA 8	a	59.0	407	—
	b	51.1	406	—

^a First heating run.

^b Second heating run.

and the apparent transition enthalpies ΔH_m are reported. The endotherms observed in the lower and higher temperature range are indicated respectively as transition I and transition II. The Table IV data show that for the random polyesteramides (PEA 1-PEA 5), the transition temperatures observed for the samples at higher amide content, fall in a temperature range typical of the melting of linear aliphatic polyamides,²⁶ whereas for the polyesteramide of high ester content, PEA 5, the first order transition occurs in the melting region of linear aliphatic polyesters.²⁶ The copolymer of intermediate composition, PEA 4, is practically amorphous. In the block copolymers PEA 6 and PEA 7, both melting transitions I and II were observed. The regularly alternating polyesteramide, PEA 8, shows one melting transition at a temperature intermediate between those of transition I and transition II.

The dynamic-mechanical data of the random polyesteramides are reported in Figures 1 and 2. In Figure 1 the complex modulus E^* is reported as a function of the temperature while the loss function, $\tan \delta$, is reported in Figure 2. The presence of a wide dissipation band in the $\tan \delta$ function, associated with a continuous decrease of the complex modulus E^* , indicates that a softening process takes place in a large temperature range. Therefore, we could not determine a definite glass transition temperature, but rather we refer to a glass transition temperature range. The lower temperature point of the glass transition range, obtained as shown in Figure 3, will be referred as "apparent glass transition temperature," T'_g . In Figures 4 and 5 are shown the dependence of the complex modulus E^* , at -80°C and $+80^\circ\text{C}$, on the sample composition and the T'_g behavior as a function of the ester content, respectively, for random polyesteram-

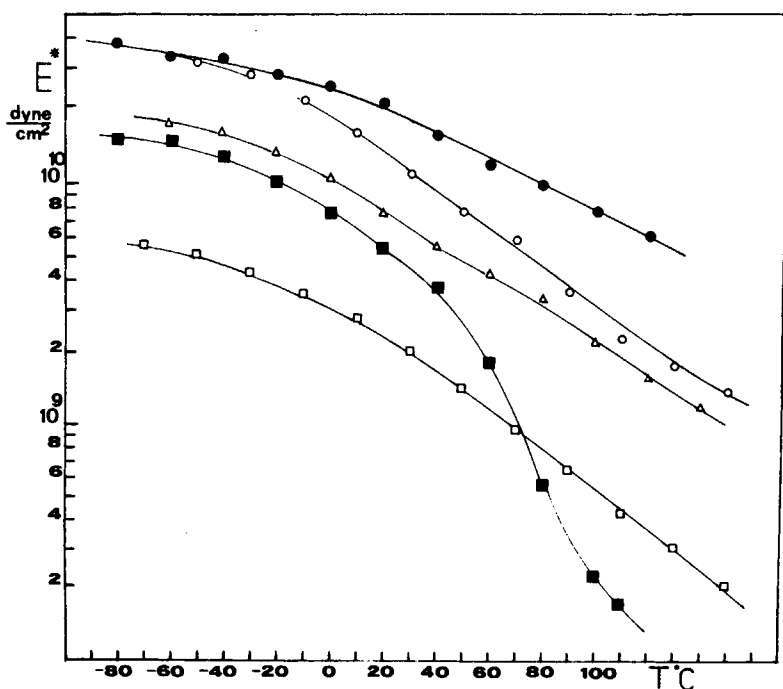


Fig. 1. Complex modulus E^* reported as a function of the temperature for the random copolymers. (●) PEA 1; (○) PEA 2; (△) PEA 3; (□) PEA 4; (■) PEA 5.

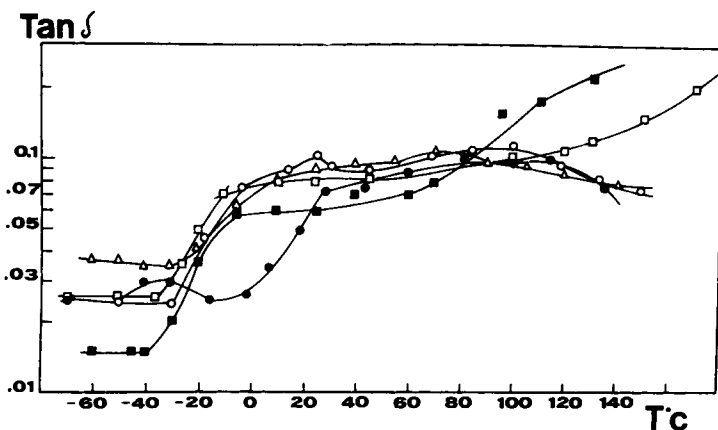


Fig. 2. Loss term $\tan \delta$ as a function of the temperature for the random copolymers. (●) PEA 1; (○) PEA 2; (Δ) PEA 3; (□) PEA 4; (■) PEA 5.

ides. In the same figures are also reported, for the sake of comparison, the values of E^* and T_g for the two homopolymers. The data concerning the pure homopolymers are those we previously reported²⁷ for the polyamide whereas, in the case of the polyester, they have been obtained from the dynamic-mechanical spectrum shown in Figure 6. In Figures 7 and 8 are reported the dynamic-mechanical spectra of the block copolymers PEA 6 and PEA 7, respectively. Significant effects due to the thermal history of the sample have been observed, and therefore we report both the spectra corresponding to the first and the second run. Finally in Figure 9 we report the data obtained for the regularly alternating polyesteramide PEA 8.

For the sake of clarity the thermal and mechanical results will be discussed following the scheme of Table I, where the copolymers are classified in three different groups on the basis of the functional groups distribution law.

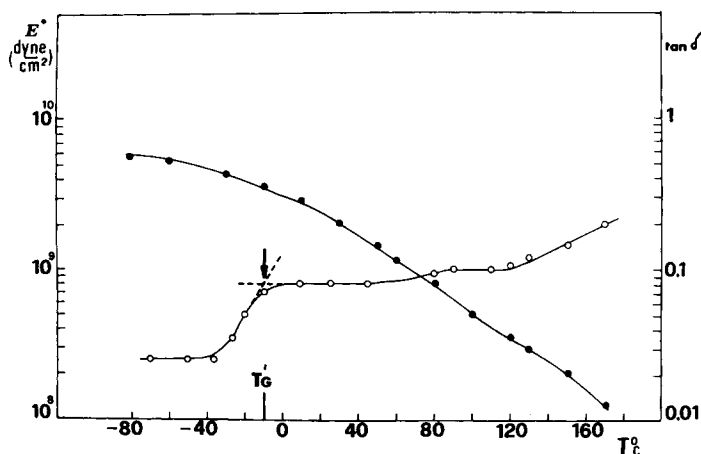


Fig. 3. Dynamic mechanical spectrum of the sample PEA 4 in which is shown the general method used to obtain the apparent glass transition, T_g .

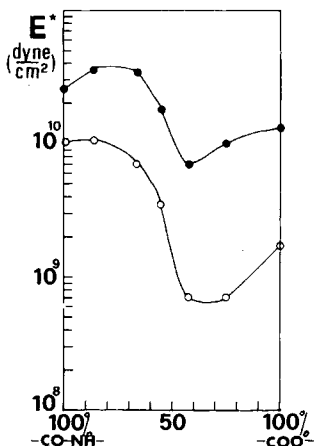


Fig. 4. Complex modulus E^* reported as a function of the chemical composition for the random samples. The two plots correspond to different isotherms. T ($^\circ\text{C}$): (●) -80 ; (○) $+80$.

Random Polyesteramides

As expected, on the basis of the general knowledge concerning polymer crystallization,²⁸ in the random copolymers the microstructural disorder hinders the crystallization process particularly for COO/CONH molar ratios near to 1, where the probability of finding homopolymer segments long enough to crystallize is very low. This is clearly shown in Table IV, where a decrease of the melting enthalpy, and consequently of the crystallinity, is observable going from the pure homopolymers (polyamide or polyester) to intermediate compositions. This feature directly influences the mechanical properties, particularly the complex modulus E^* , as shown in Figure 3. The observed minimum in the E^* value for copolymers of intermediate compositions, corresponding to the minimum in crystallinity, is attributable to a reduced filling effect arising from the rigid

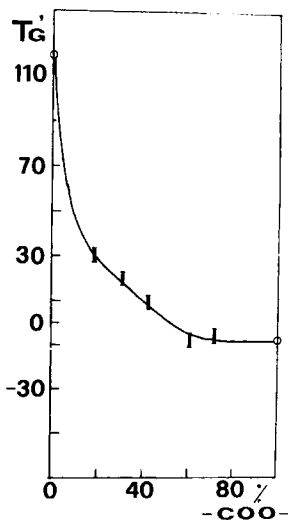


Fig. 5. Apparent glass transition temperature reported as a function of the chemical composition for random polyesteramides.

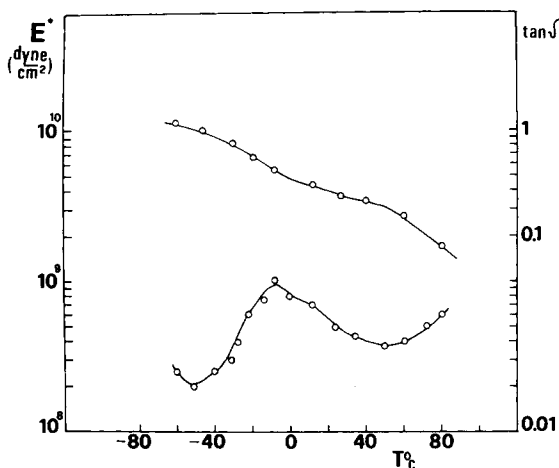


Fig. 6. Dynamic mechanical spectrum of the poly(decamethylene adipate).

crystalline regions. This minimum is more pronounced at $+80^{\circ}\text{C}$, the temperature falling between the T_g of the two homopolymers,^{27,29} while at -80°C , where every elemental volume fraction is frozen in a glassy state, this effect appears to be less relevant. Similar information may be deduced from Figure 1, and shows that the softening process is more relevant and more sharp as ester content increases; this is due to the reduced overall crystallinity in the samples of intermediate composition and to the melting of the ester crystalline phase in sample PEA 5. The T_g values also are dependent in a relevant way on the copolymer composition, showing a drastic decrease with an increase in ester content. This effect is due to the decrease of amide group and hydrogen bond concentrations in the amorphous phase, with a consequent increase of overall chain flexibility.^{30,31} Particular attention should be paid to the behavior of the loss term $\tan \delta$ as a function of the temperature (see Fig. 2). The dynamic spectra are characterized by a wide dissipation band expanded in the temperature scale. A continuous decrease of the complex modulus is associated with this band, and we

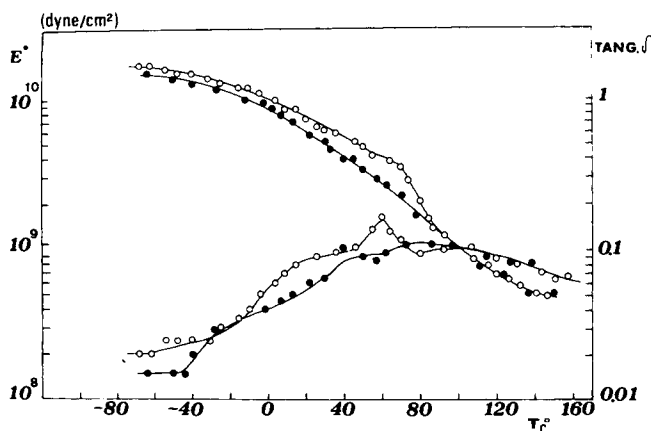


Fig. 7. Dynamic mechanical spectrum of the sample PEA 6. (○) First thermal run; (●) second thermal run.

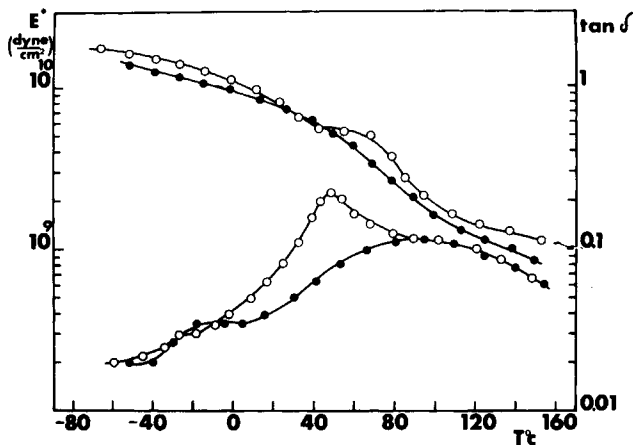


Fig. 8. Dynamic mechanical spectrum of the sample PEA 7. (O) First thermal run; (●) second thermal run.

can consider this experimental result as indicative of a glass transition widely expanded in the temperature scale. Such behavior suggests the presence of an amorphous phase where partial microsegregation takes place, thus generating a situation intermediate between those corresponding to the presence of a monophasic and a biphasic amorphous fraction,³² characterized respectively by one single sharp band and by two distinct bands. The broad bands observed are therefore due to a partial collapse of the two different bands, each typical of the two homopolymers. Similar results were observed by some authors analyzing the morphology and the mechanical properties of elastoplastic polyesteramide systems.³³

Block Polyesteramides

In copolymers having a blocklike structure two crystalline phases are present, characterized by melting temperatures typical of linear polyesters and polyamides.²⁶ However, the recrystallization of the polyester hardly seems to proceed

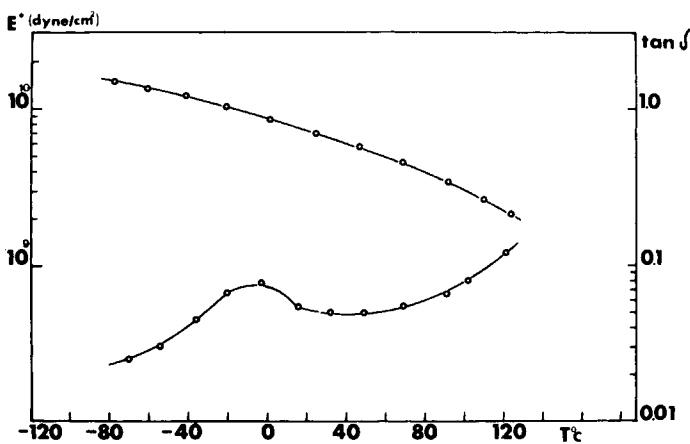


Fig. 9. Dynamic mechanical spectrum of the sample PEA 8.

after the first melting run, and this may arise from the reduced chain mobility of the polyester sequences in an environment where rigid polyamide sequences are present. This effect is also clearly evident in the mechanical results presented in Figures 7 and 8, where in the first heating run a maximum in $\tan \delta$ is present at the melting temperature of the polyester sequences, but disappears in the second run in agreement with the thermal data. The influence of the thermal history is more evident in the PEA 7 copolymer containing longer polyester sequences. Moreover, in the heating run, the shape of the $\tan \delta$ function becomes very similar to that observed for the random polyesteramides, thus indicating similar structures for the amorphous fractions.

Alternating Polyesteramide

The PEA 8 sample shows thermal and mechanical behaviors typical of an homopolymer, in agreement with its alternating chain microstructure. The values of T_m and T_g are intermediate between those of aliphatic polyesters and polyamides.

CONCLUSIONS

The main problem considered in this paper is the influence of the molecular structure on aliphatic polyesteramides physical properties. Clearly, in these systems, the molecular structure is determined by the chemical composition, (i.e., the molar ratio between amide and ester groups) and by the distribution law of monomeric units along the chain. The observed relationships between structure and physical properties give a coherent picture of the analyzed copolymers. For what concerns random and block copolymers, one or two crystalline phases, respectively, can be present, depending on the chain microstructure, while the amorphous component is characterized by a partial microsegregation of phases, generating a structure that can be considered intermediate between a monophasic and a biphasic amorphous system. The bulk properties of the alternating polyesteramide are those typical of a semicrystalline homopolymer.

References

1. T. M. Laakso and D. D. Reynolds, *J. Am. Chem. Soc.*, **82**, 3640 (1960).
2. J. L. R. Williams, J. M. Carlson, and D. D. Reynolds, *Makromol. Chem.*, **65**, 541 (1963).
3. J. L. R. Williams, T. M. Laakso, and L. E. Contois, *J. Polym. Sci.*, **61**, 353 (1962).
4. J. Preston, *J. Polym. Sci., A-1*, **8**, 3135 (1972).
5. G. Manzini, V. Crescenzi, A. Ciana, E. Ciceri, G. Della Fortuna, and L. Zotteri, *Eur. Polym. J.*, **9**, 941 (1973).
6. C. Bozzi, E. Sorta, and L. Zotteri, *Polymer*, **16**, 565 (1975).
7. G. Della Fortuna, E. Oberrauch, T. Salvatori, E. Sorta, and M. Bruzzone, *Polymer*, **18**, 269 (1977).
8. M. Cesari, G. Perego, and A. Melis, *Eur. Polym. J.*, **12**, 585 (1976).
9. P. Akcatel and B. Jasse, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1537 (1976).
10. S. Katayama, T. Murukami, Y. Takahashi, H. Serita, Y. Obuchi, and T. Ito, *J. Appl. Polym. Sci.*, **20**, 975 (1976).
11. H. R. Kricheldorf and J. Koshig, *Eur. Polym. J.*, **14**, 923 (1978).
12. K. Ateya, *Angew. Makromol. Chem.*, **7**, 79 (1969).
13. K. Dimov and Y. Georgiew, *Angew. Makromol. Chem.*, **39**, 21 (1974).

14. D. C. Allport and A. A. Mohajer, in *Block Copolymers*, D. C. Allport and W. H. Janes, Eds., Applied Science Publ., London, 1973, pp. 277-280.
15. J. M. Huet and E. Marechal, *Eur. Polym. J.*, **10**, 757 (1974).
16. J. Malescot and B. Jasse, *Bull. Soc. Chim. Fr.*, 2688 (1974).
17. G. Malescot and B. Jasse, *Eur. Polym. J.*, **11**, 669 (1975).
18. P. Huczowski and J. Kapko, *Makromol. Chem.*, **179**, 571 (1978).
19. P. Akcatel and B. Jasse, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1401 (1978).
20. G. Christoph, E. Radlmann and G. Nischk, Ger. Pat. 2,110,774 (1973); *Chem. Abstr.*, **78**, 17490t (1973).
21. T. Sato and H. Kanke, Jap. Pat. 76,125,193 (1977); *Chem. Abstr.*, **86**, 107660t (1977).
22. K. Burzin and R. Feldmann, Ger. Pat. 2,542,467 (1977); *Chem. Abstr.*, **86**, 190658S (1977).
23. P. J. Flory and F. S. Leutner, U.S. Pat. 2589688 (1952); *Chem. Abstr.*, **46**, 5861 (1952).
24. G. Maglio, C. Marchetta, A. Botta, R. Palumbo, and M. Pracella, *Eur. Polym. J.*, **15**, 695 (1979).
25. L. Castaldo, G. Maglio, and R. Palumbo, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 643 (1978).
26. J. Brandrup and E. A. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.
27. F. de Candia, G. Maglio, R. Palumbo, V. Tortorella, and V. Vittoria, *Makromol. Chem.*, **179**, 201 (1978).
28. L. Mandelkern, *Crystallization of Polymers*, McGraw-Hill, New York, 1964.
29. G. Cecere, F. de Candia, and R. Palumbo, *Makromol. Chem.*, **180**, 1037 (1979).
30. M. G. McCrun, B. E. Read, and G. Williams *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, Chap. 12.
31. A. E. Woodward, J. A. Janer, C. W. Deeley, and D. E. Kline, *J. Colloid Sci.*, **12**, 363 (1957).
32. D. S. Kaplan, *J. Appl. Polym. Sci.*, **20**, 2615 (1976).
33. G. Della Fortuna, A. Melis, G. Perego, R. Vitali, and L. Zotteri, *Proceedings of the Rubber Conference, Venice, September 1979*, p. 229.

Received March 25, 1981

Accepted November 24, 1981