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Synthesis and Characterization of Alternating Polyesteramides

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Abstract

Aliphatic and partially aromatic alternating polyesteramides were prepared from appropriate bisesteramides and aliphatic diols of various chain length. An investigation of their thermal and viscoelastic behaviour showed that the T_m and T_g values of such polyesteramides are those to be expected for a system with intermediate properties between those of the two homopolymers. A discussion of the experimental T_m values in terms of group contributions is presented.

Introduction

Several research groups (AKCATEL and JASSE,1976; KATAYAMA et al.,1976; LAAKSO and REYNOLDS,1960) have been concerned with the preparation and characterization of ordered polyesteramides,i.e., copolymers in which amide and ester groups alternate regularly along the chain, with a view to their potential use as fibres. Regularly alternating polyesteramides of the general formula : $\{CO\text{-}Ø\text{-}CONH\text{-}(CH_2)_n\text{-}NHCO\text{-}Ø\text{-}COO\text{-}(CH_2)_m\text{-}O\}_x$,conventionally referred to as nNTm, prepared from dialkylterephtalate,aliphatic diamines and diols of various chain length,have been thoroughly and extensively investigated owing to their good crystallizability and capability to be spun into fibres of high tensile strength (BORRI et al.,1975;MANZINI et al.,1973; WILLIAMS et al.,1962).

The present paper deals with the synthesis,characterization and investigation of the physico-mechanical properties of alternating polyesteramides derived from aromatic and aliphatic aminoacids, such as 4-aminobenzoic acid and ε-aminocaproic acid, aliphatic and aromatic dicarboxylic acids and aliphatic diols of various chain length. Complying with one of the main purposes of the investigation,an attempt has been made to correlate the physical properties of such copolymers with their chemical structure and composition.

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Experimental

Materials

ε-aminocaproic acid and 4-aminobenzoic acid (Fluka reagent grade) were used as received. 1,6-diaminohexane and triethylamine were purified by distillation from potassium hydroxide. Phtalic acid dichloride (Fluka technical reagent) was twice crystallized from anhydrous n-hexane under nitrogen. Adipoyl dichloride, prepared from adipic acid by treatment with thionyl chloride, was purified by vacuum distillation. The diols were distilled at reduced pressure.

Techniques

The thermal behaviour was investigated by a DSC-2 Perkin-Elmer calorimeter. The temperature scale was calibrated against pure standards. The apparent melting enthalpies, ΔH_m ,were determined by comparison of the area subtended by the melting endotherm of weighed samples of polymers, as obtained from the synthesis, with that of a weighed sample of indium.

The viscoelastic behaviour was investigated for the AC-A and AB-D polyesteramides that, by die casting, yielded films suitable for dynamic-mechanical analysis. The analysis was carried out using the Rheovibron DD II Viscoelastometer of Toyo Instruments. The viscoelastic spectra were detected at 110 Hz. The temperature range investigated was (-70°, +70°C), wide enough to observe the mechanical loss band associated with the main second order transition.

Results and discussion

a) Synthesis

The polymerization reaction was carried out using appropriate bisesteramides (compounds in which preformed amidic bonds are present), aliphatic diols and titaniumtetraisopropylate, $Ti(OC_3H_7)_4$, as the catalyst, according to the following reaction scheme:

$$\begin{array}{l} C_2H_5OCO\text{-}R\text{-}NHCO\text{-}R'\text{-}CONH\text{-}R\text{-}COOC_2H_5 \quad + \quad 2\ HO\text{-}R''\text{-}OH \longrightarrow \\ HO\text{-}R''\text{-}OCO\text{-}R\text{-}NHCO\text{-}R'\text{-}CONH\text{-}R\text{-}COO\text{-}R''\text{-}OH \quad + \quad 2\ C_2H_5OH \qquad (I) \\ \qquad\qquad\qquad (\ A\ ) \end{array}$$

$$x\ A \longrightarrow \left\{ CO\text{-}R\text{-}NHCO\text{-}R'\text{-}CONH\text{-}R\text{-}COO\text{-}R''\text{-}O \right\}_x \quad + \quad x\ HO\text{-}R''\text{-}OH \qquad (II)$$

In stage (I), the ethoxy groups of the bisesteramide are substituted for by the diol to give the bis(hydroxyalkyl)diester (A), which at higher temperature and under vacuum (stage II) forms the wanted polyesteramide by diol elimination.

Attention was essentially focused on two types of polymers: aliphatic and partially aromatic polyesteramides, depending on the nature of the bisesteramides used, aliphatic diols being used in every case. Bisesteramides of general formula $C_2H_5OCO\text{-}R\text{-}NHCO\text{-}R'\text{-}CONH\text{-}R\text{-}COOC_2H_5$ were prepared to high yields by a Schotten-Baumannn reaction carried out in chloroform, by using an acid dichloride and the appropriate aminoacid ethylester in the presence of triethylamine:

$$2\ C_2H_5OCO\text{-}R\text{-}NH_2 \ + \ ClOC\text{-}R'\text{-}COCl \ \xrightarrow[N(CH_3)_3]{T<0°C}$$

$$C_2H_5OCO\text{-}R\text{-}NHCO\text{-}R'\text{-}CONH\text{-}R\text{-}COOC_2H_5 \ + \ 2\ HCl$$

$R = -(CH_2)_5- \ ; \ -C_6H_4-$

$R' = -(CH_2)_4- \ ; \ -C_6H_4- \ ; \ -(CH_2)_{10}-$

The bisesteramides prepared are listed in Table 1.

TABLE 1

Bisesteramides prepared, of the general formula EtOCO-R-NHCO-R'-CONH-R-COOEt

Code	R	R'	Yield (%)	T_m (°C)	Crystallization solvent
AC-A	$-(CH_2)_5-$	$-(CH_2)_4-$	92	113-114	Toluene
AC-T	$-(CH_2)_5-$	$-C_6H_4-$	93	153-154	Acetone/Toluene
AB-D	$-C_6H_4-$	$-(CH_2)_{10}-$	93	179-180	DMSO/Ethanol

The various series of regularly alternating polyesteramides were prepared by reacting the appropriate bisesteramides with aliphatic diols of different chain length, $HO\text{-}(CH_2)_n\text{-}OH$, n = 2,4,6....12. The polymers prepared are listed in Table 2.

Different polymerization temperatures were selected, depending on the T_m of the bisesteramides. A short reaction time in stage II was required to avoid randomness by exchange between ester and amide groups. Experimental details have been reported elsewhere (CASTALDO et al.,1982). The polymers prepared are white opaque or light coloured, soluble in the typical solvents of polyamides,

TABLE 2

Preparation and characterization of polyesteramides

Code	Polymeriz.temp.(°C) a)		b) η_{inh}	c) T_m	d) ΔH_m
	stage I	stage II	(dL/g)	(°C)	(J/g)
AC-A2	200-210	240-250	0.65	163	36
AC-A4	" "	" "	0.71	156	36
AC-A6	" "	" "	0.67	147	36
AC-A8	" "	" "	0.40	140	34
AC-A10	" "	" "	0.87	137	36
AC-A12	" "	" "	0.47	134	33
AC-T2	210-220	250-260	0.31	204	22
AC-T4	" "	" "	0.58	190	42
AC-T6	" "	" "	0.54	177	43
AC-T8	" "	" "	0.45	167	41
AC-T10	" "	" "	0.48	166	38
AC-T12	" "	" "	0.99	163	36
AB-D2	230-240	260-270	0.52	242	26
AB-D4	" "	" "	0.49	192	27
AB-D6	" "	" "	0.50	190	27
AB-D8	" "	" "	0.56	188	26
AB-D10	" "	" "	0.48	171	25
AB-D12	" "	" "	0.47	167	25

a) Polymerization time: stage I, 4 h; stage II, 1 h

b) In m-cresol at 25°C; c = 0.5 g/dL

c) Estimated reproducibility: ± 0.5°C

d) Estimated reproducibilty : ± 2 J/g

swollen in chlorinated polar solvents, and insoluble in solvents suitable for polyesters, thus indicating that their solubility is markedly affected by the amidic groups,i.e., by the presence of hydrogen bonds. The inherent viscosity values are comparable with those reported in the literature for analogous polymers. The infrared spectra exhibit the characteristic absorption bands of ester and amide carbonyls (1735,1640,1535 and 650 cm^{-1}). The presence of a band at 3305 cm^{-1} together with the absence of a shoulder at 3448 cm^{-1}, attributable to free -NH absorption, is evidence of $\simeq$100 hydrogen bonding.

b) Thermal properties

All copolymers prepared are semicrystalline materials showing a first order transition, as revealed by DSC investigations,in the temperature range 134-242°C. The apparent melting enthalpies, ΔH_m, (see Table 2) are generally quite similar for varying diol length within each series, while they depend on the chemical constitution of the parent bisesteramides. Differences in crystallinity of the polyesteramides investigated should not however be very substantial. The melting temperatures T_m of the polyesteramides of the three series are plotted in Figure 1 as a function of the number of carbon atoms of the diol.

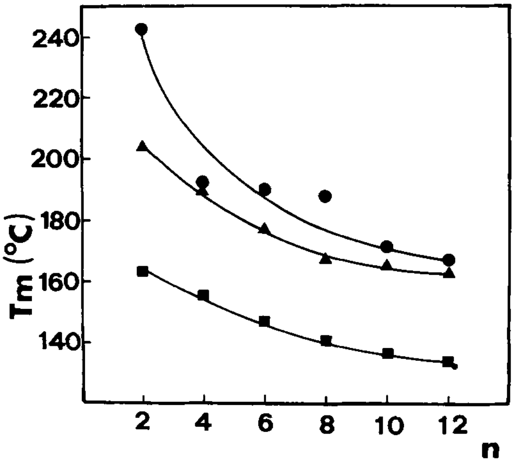

Figure 1. Dependence of T_m of the prepared polyesteramides on the number of-CH_2- groups of the diol,n. (● AB-D; ▲ AC-T; ■ AC-A)

As expected,partially aromatic polyesteramides show higher melting temperatures than the aliphatic ones,and,within each series, T_m is a regularly decreasing function of the number of -CH_2- groups in the diol. The differences in melting temperatures between aliphatic and aromatic polyesteramides are not however as large as could have been expected from predictions based on semi-empirical rules. In fact,by using the relation: $(\sum_i Ym_i)/Z$, where Ym_i are the group contributions to T_m, and Z is the number of atoms linked in the backbone repeat unit, and by assuming for Ym_i the values found in the literature (VanKREVELEN,1972) for polyamide and polyester homopolymers, we obtained good agreement between experimental and calculated T_m values for AC-A polyesteramides only, while for partially aromatic polymers the experimental values are 10-to-70°C lower than calculated. Quite similar results were also obtained by using the above relation for other classes of alternating polyesteramides reported by other authors (LAAKSO and REYNOLDS, 1960; KATAYAMA et al.,1976). It would thus appear that T_m predictions based on group contributions reported for homopolymers cannot be applied to ordered polyesteramides that have rigid aromatic groups also in the chain repeat unit.

c) Viscoelastic behaviour

The viscoelastic behaviour observed was similar in all samples analysed and is characterized by a single band in the tanδ function. The general trend is illustrated in Figure 2, where the viscoelastic spectra of AC-A4,AC-A6 and AC-A10 polyesteramides are shown as an example.

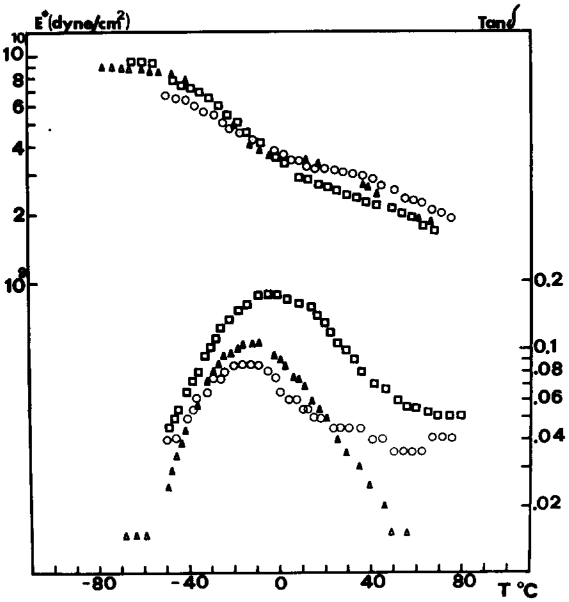

Figure 2. Dynamic-mechanical spectra of AC-A samples (○ AC-A4; □ AC-A6; △ AC-A10)

The behaviour observed for both tanδ and the complex modulus E^* are related to the glass transition T_g, which can be taken as the temperature where tanδ is a maximum (Mc CRUM et al.,1967). This temperature falls in a range where a sharper decrease of $E^*$is also observed. The data of Figure 2 yield T_g values of -15°C, -7°C and -12°C for the sample having n = 4,6,and 10 respectively.
Samples of the AB-D series show T_g values close to 0°C, slightly higher than those found for AC-A series. These findings are evi-

dence of the fact that, in terms of chain flexibility,the presence of two rigid aromatic groups in the chain repeat unit of AB-Dn polyesteramides is partially balanced by the long flexible paraffinic sequences of the dodecandioic acid. Thus,as a first approximation,neglecting the observed small differences in crystallinity, the differences in chemical constitution do not seem to affect in a relevant way the physical behaviour. As a matter of fact, in the samples investigated of the AC-A and AB-D series, the T_g values fall in the range (-15°, +15°C). These T_g values are intermediate between those generally observed in aliphatic polyester and polyamide homopolymers (BRANDRUP and IMMERGUT,1975).

Taking (-50°, -20°C) and (+60°, +90°C) as the typical T_g ranges of the linear homopolymers (as obtained from dynamic measurements), and assuming a 1:1 composition for the polyesteramides, we applied the Fox equation (FOX,1956) to the results obtained. Such calculation give T_g values in the range (-6°, +24°C), which,particularly in view of the approximation introduced, may be deemed fairly close to the experimental values. The physical behaviour is therefore in keeping with that expected of a semi-crystalline system with intermediate properties between those of aliphatic polyesters and polyamides. As a matter of fact,the viscoelastic behaviour observed is indicative of a homogeneous amorphous component and the thermal data show the presence of a single crystalline phase; the T_g and T_m values are intermediate between those of the two pure homosystems. These findings are consistent with the regularly alternating chain structure and they are wholly at variance with results obtained on blocklike and random polyesteramides (CASTALDO et al.,1982), whose physical behaviour is affected by incompatibility phenomena and phase separation of the two homocomponents.

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