Block/segmented polymer: 2. Studies on the thermal and mechanical properties of poly(amide ester)-ester copolymer

Sureschandra Bera*
Polymer Group, Regional Research Laboratory (CSIR), Trivandrum-695 019, India

and Zbigniew Jedlinski
Institute of Physical Chemistry and Polymer Technology, Silesian Technical University Gliwice, Poland

(Received 6 June 1991; revised 13 December 1991; accepted 16 December 1991)

A new poly(amide ester)-ester copolymer was synthesized by reacting two oligomers, namely, oligo(amide ester) and oligo ester. Depending on the molar ratio of the two oligomers, a behavioural pattern of elastomeric to elastoplastic material was observed. D.s.c. studies revealed two glass transition temperatures: one at −40 to −50°C and another at 40 to 50°C, showing the presence of two different segments in the polymer backbone. Electron microscopic studies could not distinguish and differentiate the phase separation behaviour of the segments in the polymer. Mechanical studies showed that the polymer has a tensile strength at break of 6–20 MPa with an elongation as high as 160%.

(Keywords: block/segmented polymer; oligomer; glass transition temperature; mechanical properties; tensile; elongation; recovery)

INTRODUCTION

Amide-ester copolymers have become a topic of interest in recent years due to their unique thermomechanical properties[1]. A class of amide ester polymers have been randomly arranged in the chain, exhibiting properties intermediate between those of polyamides and polyesters[2]. An approach has been adopted here to produce a regular block/segmented (amide ester)-ester copolymer by reacting two oligomers, namely, oligo(amide ester) (A) as the hard block/segment and oligo ester (B) as the soft block/segment[3,4]. This type of (amide ester)-ester copolymer is expected to exhibit dynamic mechanical properties over a large range of working temperature. Some interesting properties like controlled biodegradability and specific absorption/diffusion are also expected.

Barrows[5] reported that the reaction between a diamine and hydroxy acid could lead to a monomer amido diol with two amide units. Jedlinski *et al.*[6,7] reported that the same amido diol can be synthesized by the ring opening reaction of lactones with diamines, with the advantage of single stage operation and yield and purity above 90%. Bera[8] synthesized various amido diols from lactones and diamines in the presence of isopropanol. The amido diols synthesized were used in the preparation of a number of oligo(amide ester)s with different molecular sizes. Some of these oligo(amide ester)s were transesterified with oligo esters, prepared separately, to obtain the final block/segmented (amide ester)-ester copolymer, as shown in *Figure 1*.

In this paper we report the physico-mechanical and thermal behaviour of oligo(amide ester) oligomers and of the final block/segmented poly(amide ester)-ester copolymers with some possible applications in biomaterials.

EXPERIMENTAL

Materials

γ-Butyrolactone (Merck, Schuchardt, Germany) and hexamethylene diamine (Fluka AG, Switzerland) were used without further purification. Various dicarboxylic acids, namely adipic, sebacic and dodecanedioic acid, were supplied by Reachim, Russia and Aldrich Chemicals, Germany.

Oligo(amide ester) and oligo ester were synthesized in the laboratory and purified to remove by-products and unreacted species before analysis. The poly(amide ester)-ester copolymer was characterized without using any separation techniques.

Chemical analysis

The amine ($-NH_2$), hydroxyl ($-OH$) and carboxyl ($-COOH$) functionalities of the monomer were quantitatively measured; the carboxylic groups were measured by standard titration[9] and the hydroxyl groups by treatment with anhydride in pyridine followed by the determination of the anhydride used in the case of oligo ester. For oligo(amide ester), since it is insoluble in common solvents, i.r. spectroscopy was used for the first time to determine the hydroxyl functionalities by taking the amide diol as the reference. The hydroxyl peak signal at 3300 cm^{-1} of the amido diol (known hydroxyl

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*To whom correspondence should be addressed

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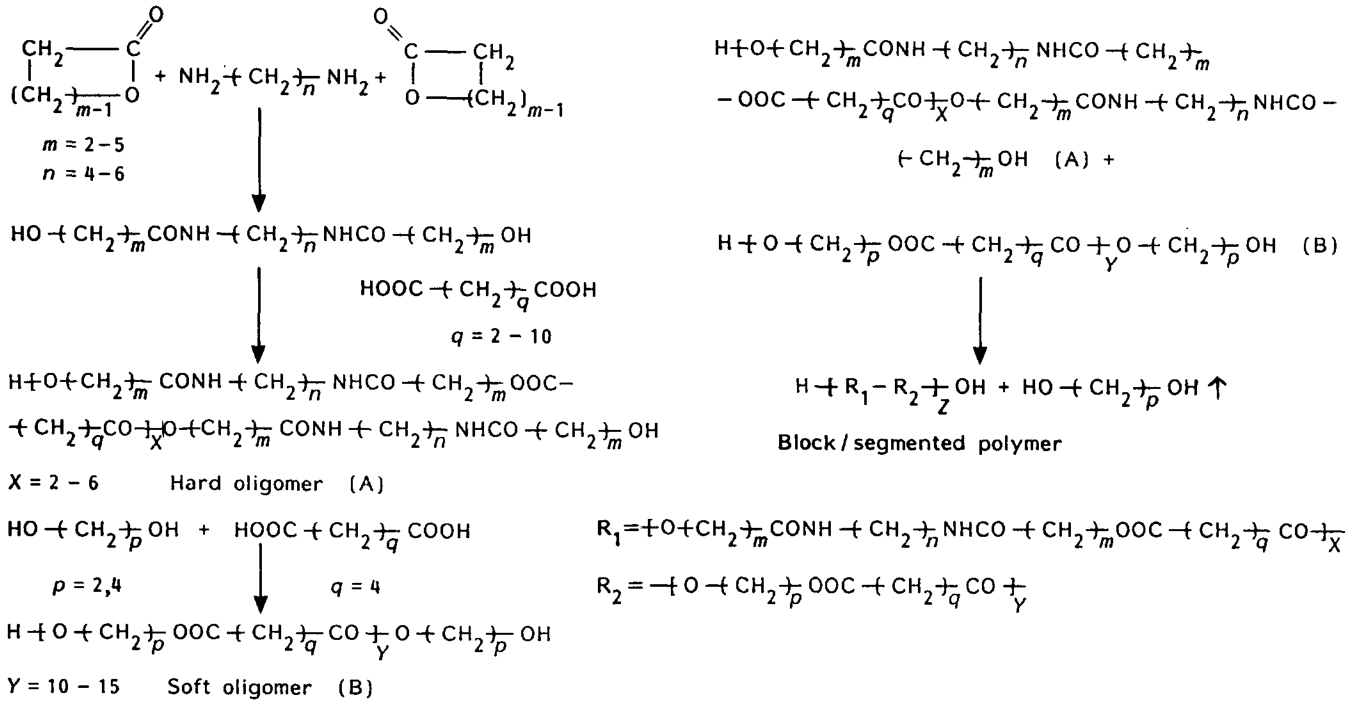

Figure 1 Preparative scheme of poly(amide ester)-ester copolymer starting from lactone

functionalities) and the oligo(amide ester) diol were compared, to determine the hydroxyl functionalities of the oligomer. The temperature of the i.r. cell holder and the deposited sample film thickness were kept constant[3]. The i.r. spectra were obtained using a Specord M-80 spectrophotometer (Carl Zeiss, Jena, Germany).

Thermal analysis

Thermal stability of the oligomer was studied by t.g.a. and d.t.a. using a Q-1500 DMOM Derivatograph (Budapest, Hungary). The glass transition temperature (T_g) and melting temperature (T_m) were determined by d.s.c. using DSC 1090 OB Dupont apparatus.

Solution behaviour

The solution behaviour of oligomers and polymers was studied by placing ~0.1 g powdered sample in the case of oligomer and 0.05 g in the case of the polymer in 100 ml solvent in a conical flask and allowing the mixture to stand in a mechanical stirrer for 24 h at room temperature (20–25°C). In the case of insolubility, the temperature was increased to the reflux temperature of the corresponding solvent and swelling or solubility was carefully observed. Swelling at room temperature or at reflux temperature with the corresponding solvent was reported as partially soluble whereas fully soluble either at room temperature or at the reflux temperature was reported as soluble.

Viscosity was measured by using a Ubbelohde viscometer (22370/009984) in a thermostatically controlled water bath. Inherent viscosity was measured by taking 0.5 g of the sample in 100 ml of *m*-cresol at a temperature of 20 ± 0.5°C.

Mechanical test

Tensile stress, strain and modulus of the film developed from the poly(amide ester)-ester polymer, were determined using a mechanical tester (Instron Corporation, series IX, Automated Materials Testing System) with the following parameters: cross-head speed 5.00 mm min^{-1}; humidity 50%; temperature 23°C. The dimensions of the samples tested were: thickness 0.05–0.15 mm; width 10.00 mm; gauge length 40.00 mm; specimen GL 100.00 mm. Three samples were tested and the mean values were recorded.

Electron microscopy

A very thin sample (500–1000 Å thick) was cast from dimethylformamide (DMF) solution at 100°C and kept under vacuum for 24 h. The domain structure was observed using an electron microscope (JEM 120, JEOL, Japan).

Preparation of monomer, oligomer and polymer

The monomer amido diol was prepared from the reaction of lactone with diamine at room temperature. Amido diol was reacted with dicarboxylic acid in the presence of Sb_2O_3 as catalyst and Irganox-1076 as antioxidant to obtain oligo(amide ester) as the hard oligomer. A molar excess of amido diol gave hydroxyl-terminated oligomer, whereas the hydroxyl-terminated oligo ester (soft oligomer) was prepared using a method reported elsewhere[10].

The preparation of poly(amide ester)-ester copolymer involved transesterification between two oligomers, oligo(amide ester) and oligo ester, in the presence of Sb_2O_3 and Irganox-1076. A hard, tough polymer was collected from the reactor in the form of a solution in DMF under hot conditions.

Film preparation

The polymer solution in DMF (10% w/w) was removed from the reactor and put on a glass plate mould. DMF was allowed to evaporate in an oven controlled at 100°C for 30–45 min to form a brownish transparent film. Finally the film was kept inside the oven at 80–90°C for an additional 24 h under vacuum.

RESULTS AND DISCUSSION

Molecular phenomenon of oligomer and polymer

Due to the insolubility of the hard oligo(amide ester) and poly(amide ester)-ester copolymer in common organic solvents it was not possible to characterize them using n.m.r. spectroscopy. However, the existence of the amide ester signal in i.r. spectra has been previously reported[3]. Due to insolubility, the average molecular weight was not determined by the conventional method. The hydroxyl end group was estimated by i.r. spectroscopy for the first time and thus the number-average molecular weight ($\bar{M}_n$) of the hard oligomer was determined whereas the hydroxyl signal from i.r. spectroscopy was not very prominent in the case of poly(amide ester)-ester copolymer, perhaps due to the interaction of carboxyl and amide stretching. Therefore, in the present investigation the polymer is reported to have an inherent viscosity varying from 1.55 to 1.75 dl g^{-1}, whereas for hard oligomers, the inherent viscosity was 0.16–0.22 dl g^{-1}.

However, the solubility of oligomers and polymers in different solvents (*Table 1*) has shown that DMF is ideal for casting film from solution. The film is thus an indication of the high molecular weight of the polymer which is confirmed by the mechanical properties.

Table 1 Solubility behaviour of poly(amide ester)-ester copolymer[11]

	Solvents	Solubility parameter ($cal^{1/2}$ $cm^{3/2}$)	Hydrogen bonding index	Solubility of polymer[a]
1	Tetrahydrofuran	9.1		–
2	Benzene	9.2		–
3	Chloroform	9.3	2.2	–
4	Ethylmethyl ketone	9.45	5.0	–
5	Chlorobenzene	9.50		–
6	Acetone	9.62	5.7	–
7	*m*-Cresol	10.2		+
8	Pyridine	10.7		–
9	Dimethyl acetamide	10.8		±
10	*N*-methylpyrrolidone	11.3	5.6	±
11	Isopropanol	11.5		–
12	Dimethylformamide	12.1		±
13	Formic acid	12.1		+
14	H_2SO_4			+

[a] +, Soluble; –, insoluble; ±, soluble at reflux temperature of the solvent

Mechanical properties

The present study is restricted to using the monomer bis(hydroxy butyro amide)hexane prepared from γ-butyrolactone and hexamethylene diamine, where the amide unit spacer remains constant and the ester group spacer is varied in the dicarboxylic acid. Three acids, adipic acid (four CH_2 units), sebacic acid (eight CH_2 units) and dodecanedioic acid (10 CH_2 units), were used to study the spacer effect on oligomer properties and on the final polymer properties.

For the following reaction conditions of a molar ratio of dicarboxylic acid to amido diol of 1:1.05, Sb_2O_3 catalyst (0.1% w/w) and antioxidant (Irganox 1076, 0.1% w/w) varying molecular weight and viscosity of the hard oligomer were noticed whereas T_g and T_m were found to be similar (*Table 2*).

Soft oligo esters were prepared by varying the mole ratio of acid and diol. White, waxy solids, semi-liquid in nature, were observed with T_gs close to each other and T_m varying with variation in molecular weight (*Table 3*).

In a single system (A_1-B_3), variation of molar and weight fraction of the oligomers has been studied to obtain the properties of the final polymer (*Table 4*). All the hard oligo(amide ester)s (A_1, A_2 and A_3) have undergone transesterification with soft oligo esters (B_1, B_2 and B_3), using a molar ratio of 1:1 (*Table 5*).

The number of methylene units in the dicarboxylic acid has been seen to alter the mechanical properties (*Figure 2*). Although the inbuilt amide unit in the starting amido diol is kept at constant methylene spacings, use of different acid, i.e. variation of the CH_2 unit from two ester linkages, has given rise to varying modulus (*Figure 3*) and tensile stress. With constant methylene length, a hard oligomer (A_1) has been reacted with a soft oligomer (B_3), and the variation of tensile stress and modulus against the hard block weight and mole fraction has been plotted (*Figure 4*). As the hard oligomer content decreases, stress starts decreasing, but at a mole fraction of hard oligomer of 0.478–0.557, increase in stress

Table 2 Characteristics of hard segment forming oligomer oligo(amide ester) diol

$\mathrm{HO[(CH_2)_{\overline{m}}CONH(CH_2)_{\overline{x}}NHCO(CH_2)_{\overline{m}}OOC(CH_2)_{\overline{n}}CO]_{\overline{X}}O(CH_2)_{\overline{m}}CONH(CH_2)_{\overline{x}}NHCO(CH_2)_{\overline{m}}OH}$ $X = 2–6$

Oligomer	Average hydroxyl equivalent/ per 100 g[a]	$\bar{M}_n$ (end group analysis)	Inherent viscosity (dl g^{-1})[b]	Glass transition temperature (°C)[c]	Melting temperature (°C)[c]
A_1 $x = 6$ $m = 3$ $n = 4$	0.1860	1050	0.162	43	196
A_2 $x = 6$ $m = 3$ $n = 8$	0.1432	1369	0.215	43	186
A_3 $x = 6$ $m = 3$ $n = 10$	0.1377	1437	0.225	41	189

[a] Measured from i.r. spectroscopy

[b] Viscosity determined using *m*-cresol at 20 ± 0.5°C (concentration 0.5 g per 100 ml)

[c] By d.s.c.

Table 3 Characteristics of soft segment forming oligomer oligo ester diol

$H-[O-(CH_2)_m-OOC-(CH_2)_n-CO-]_Y-O-(CH_2)_m-OH$

$Y = 10-15$

Oligomer	Molar ratio of acid to diol	Carboxyl equivalent	Hydroxyl equivalent (mg KOH g^{-1} sample)^a	$\bar{M}_n$ (end group analysis)	$\bar{M}_n{}^b$	$\bar{M}_w/\bar{M}_n{}^c$
B_1 $m = 2$ $n = 4$	1:2.00	Nil	145.67	770	980	1.52
B_2 $m = 2$ $n = 4$	1:1.50	Nil	65.67	1700	1500	1.46
B_3 $m = 2$ $n = 4$	1:1.25	Nil	44.00	2550	3000	1.37

[a] By end group analysis
[b] By vapour pressure osmometry
[c] By g.p.c.

Table 4 Physico-mechanical behaviour of poly(amide ester)-ester copolymer

$-(A-B-A)_n/-(A-B)_n/-(B-A-B)_n$

Hard oligomer (A_1), soft oligomer (B_3)

Sample	Weight fraction of hard oligomer	Molar fraction of hard oligomer	Appearance of film	Stress at break (MPa)	Strain at break	Stress at yield (MPa)	Strain at yield	Modulus (MPa)
P_1	0.660	0.834	Opaque	19.071	0.071	15.440	0.0530	606.08
P_2	0.571	0.770	Opaque	10.155	0.047	9.258	0.0450	429.50
P_3	0.500	0.718	Opaque	10.612	0.046	0.155	0.0357	447.85
P_4	0.392	0.619	Opaque	8.056	0.118	7.499	0.0809	224.44
P_5	0.363	0.590	Translucent	8.037	0.258	0.035	0.0368	164.76
P_6	0.333	0.557	Transparent	9.584	1.265	0.874	0.0173	51.34
P_7	0.281	0.497	Transparent	12.199	1.160	1.661	0.0148	170.64
P_8	0.266	0.478	Transparent	13.128	0.740	6.445	0.0642	249.89
P_9	0.250	0.456	Transparent	10.338	0.374	5.572	0.0331	223.35
P_{10}	0.200	0.386	Transparent	10.365	1.450	0.936	–	69.93
P_{11}	0.090	0.201	Translucent	10.565	1.590	–	–	–

Table 5 Physico-mechanical behaviour of poly(amide ester)-ester copolymer

Sample	Appearance of film	Stress at break (MPa)	Strain at break	Stress at yield (MPa)	Strain at yield	Modulus (MPa)
P_{12} (A_1-B_1)	Opaque	6.045	1.120	0.215	0.0152	152.62
P_{13} (A_2-B_1)	Opaque	7.520	1.056	1.526	0.0136	105.25
P_{14} (A_3-B_1)	Opaque	6.750	1.092	7.460	0.0245	80.96
P_{15} (A_1-B_2)	Translucent	10.455	1.452	9.266	0.0146	165.45
P_{16} (A_2-B_2)	Transparent	12.352	1.526	8.570	0.0215	225.28
P_{17} (A_3-B_2)	Transparent	12.264	1.550	7.212	0.0175	250.54
P_{18} (A_1-B_3)	Transparent	15.233	1.562	10.045	0.0132	176.28
P_{19} (A_2-B_3)	Transparent	18.540	1.652	9.350	0.1250	230.85
P_{20} (A_3-B_3)	Transparent	18.962	1.590	9.775	0.0142	212.36

Molar ratio of A to B is 1:1 (on the basis of hydroxyl functionality)

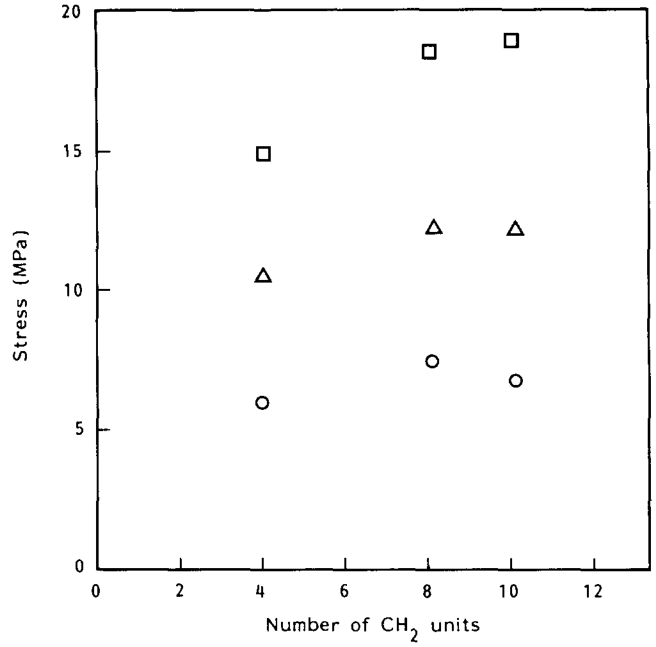

Figure 2 Variation of tensile stress of poly(amide ester)-ester copolymer *versus* the number of CH_2 units between two adjacent ester groups of oligo(amide ester): (○) oligoester B_1; (△) oligoester B_2; (□) oligoester B_3

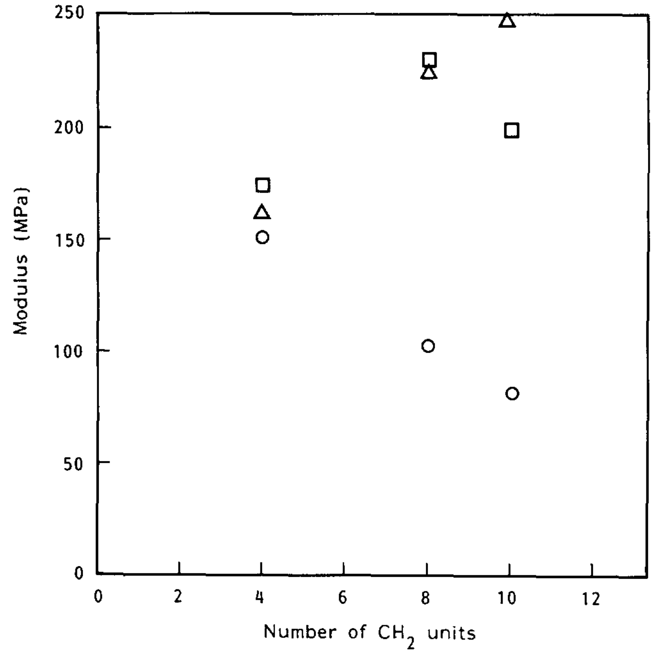

Figure 3 Variation of tensile modulus of poly(amide ester)-ester copolymer *versus* the number of CH_2 units between two adjacent ester groups of oligo(amide ester): (○) oligoester B_1; (△) oligoester B_2; (□) oligoester B_3

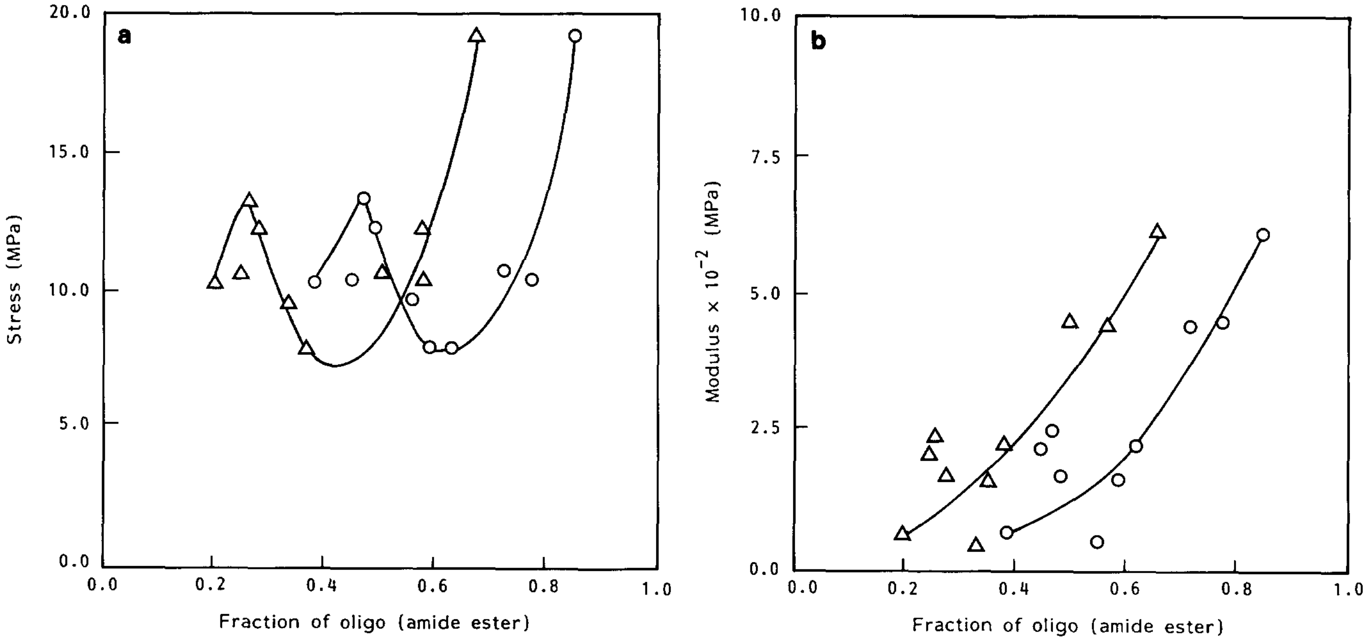

Figure 4 Variation of (a) tensile stress and (b) modulus of poly(amide ester)-ester copolymer against the fraction of oligo(amide ester): (○) mole fraction; (△) weight fraction

(10–12 MPa) has been recorded, whereas the modulus in all cases gradually decreases as the hard oligomer fraction decreases. In general, the stress–strain behaviour at different weight fractions of hard oligo(amide ester) content in the copolymer shows a decrease in stress and an increase in elongation as the hard oligomer content decreases. The static mechanical properties, however, have shown the copoly(amide ester)-ester to be a tough elastoplastic polymeric material.

Microscopic analysis

Microscopic analysis has been carried out on very thin films (500–1000 Å) cast from DMF of three poly(amide ester)-ester copolymers with hard to soft oligomer molar ratios of 1:1 P_{18}, P_{19} and P_{20} with the highest tensile stress and elongation, keeping in mind that phase separation of the two blocks/segments would have been possible. Not surprisingly, very little existence of microphase separation is seen due to the mutual

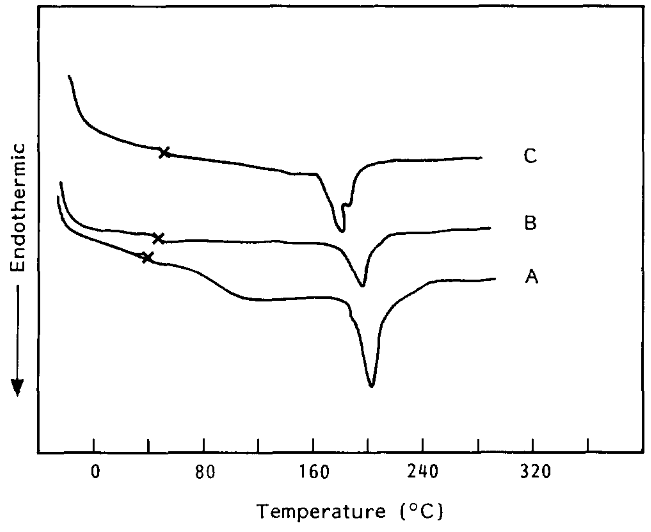

Figure 5 D.s.c. curves of oligo(amide ester) oligomers (heating rate 20°C min^{-1}): (A) sample A_1 (5.0700 mg); (B) sample A_2 (4.7662 mg); (C) sample A_3 (4.4449 mg)

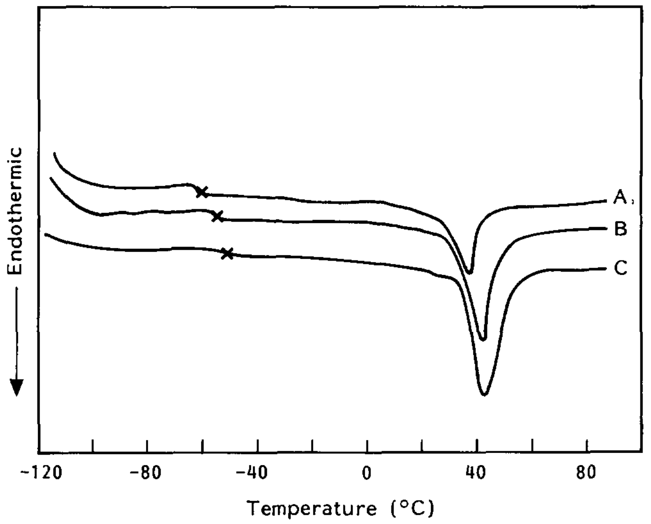

Figure 6 D.s.c. curves of oligoester diol oligomers (sample size <10 mg, heating rate 20°C min^{-1}): (A) sample B_1; (B) sample B_2; (C) sample B_3

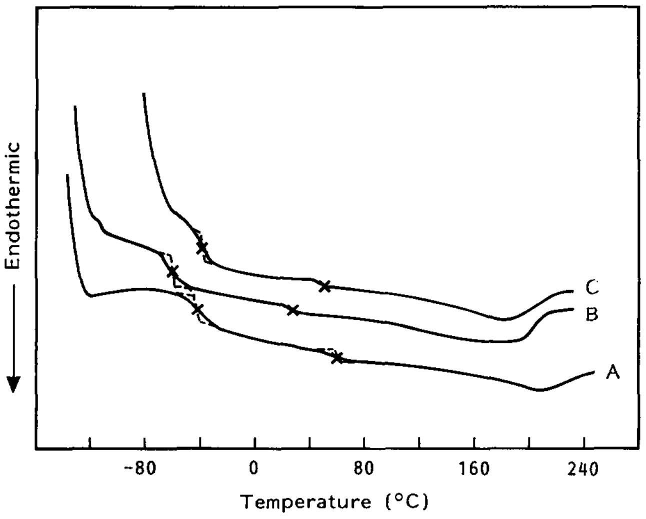

Figure 7 D.s.c. curves of poly(amide ester)-ester copolymers (sample size <10 mg, heating rate 20°C min^{-1}): (A) sample P_{18}; (B) sample P_{19}; (C) sample P_{20}

compatibility of (ester amide) to ester segments in the final polymer. The presence of hydrogen bonding between two adjacent amide ester groups and the smaller size of the block would have been major factors in preventing phase separation. However, future work is underway to study microphase-separated amide ester copolymer with oligomers of increasing molecular size.

Thermal studies

This was attempted by developing two hard and soft oligomers with T_gs and T_ms ($\sim$200°C) as high as possible from ambient temperature. The soft oligo ester had a T_g as low as possible (-40 to -50°C). The thermal behaviour of the two oligomers is incorporated into the final polymer in such a way that the same behaviour is seen (*Figures 5* and *6*). From d.s.c. studies of the poly(amide ester)-ester copolymer, the presence of two oligomeric segments/blocks is identified with only one endotherm for the hard block amide ester melting at and above 200°C whereas two T_gs (-40 to -50°C and 40 to 50°C) are prominent (*Figure 7*).

CONCLUSIONS

Block/segmented (amide ester)-ester copolymer exhibits tough elastoplastic behaviour. Two T_gs (-40 to -50°C and 40 to 50°C) and a T_m at $\sim$200°C show that the polymer can be used in a wide working temperature range. The poly(amide ester)-ester film, cast from solution, has shown fairly high mechanical properties which can be used in specific fields where a combination of biocompatibility and biodegradability is expected. Moreover, through this oligomeric reaction, a liquid crystalline polymer with a soft oligomer as the flexible spacer could be developed more easily.

ACKNOWLEDGEMENT

Thanks are due to the Ministries of Education, Governments of India and Poland for granting the Polish Government Fellowship without which this work would not have been possible.

REFERENCES

1 Noshay, A. and McGrath, J. E. 'Block Copolymers Overview and Critical Survey', Academic Press, New York, 1977
2 Goodman, I. 'Developments in Block Copolymers-1', Applied Science, London, 1982
3 Bera, S. and Jedlinski, Z. *J. Polym. Sci.* in press
4 Pelc, R., Kaczmarczyk, B., Knopik, H., Marks, R. and Bera, S. 'Sprawozdanie, Zaktad Polimerow', PAN, Zabrze, 1989 (in Polish)
5 Barrows, T. H. 2nd International Conference on Polymers in Medicine, Capri, Italy, 1985, Reprints
6 Jedlinski, Z., Kowalczuk, M. and Kurcok, P. *Macromol. Chem. Macromol. Symp* 1986, **3**, 277
7 Brandt, K. and Latawiec, T. *Bull. Polish Acad. Sci. Chem.* 1989, **3–4**, 45
8 Bera, S. *PhD Thesis* Silesian Technical University, Poland, 1990
9 Collins, E. A., Bares, J. and Billmeyer Jr, F. W. 'Experiments in Polymer Science', John Wiley and Sons, New York, 1973
10 Sorenson, R. W. and Campbell, T. W. 'Preparative Methods of Polymer Chemistry', Interscience Publishers Inc., New York, 1961
11 Burrel, H. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), Intersciences, New York, 1975, p. 337