polymer communications

Polysulphone-arylate block copolymers

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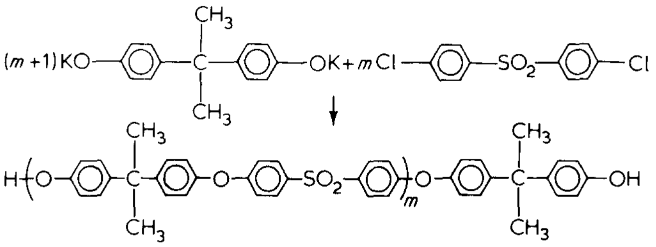
A number of block copolymers have been prepared and characterized[1]. However, most attention has been given to elastomeric copolymers and little fundamental work has been reported on glassy block copolymer systems. Polyaryl ethers such as polysulphone prepared from bisphenol-A and 4,4'-dichlorodiphenylsulphone is highly heat-resistant and has useful properties[2]. In addition polyarylates (polyesters of different aromatic dicarboxylic acids and dihydric phenols) are interesting new thermoresistant polymers[3]. It is thus of interest to see if the polyaryl ether segments can combine with polyarylate units to form a new polymer molecule. This paper deals with the synthesis and characterization of some polysulphone–arylate block copolymers which have not previously been reported.

The low molecular weight dihydroxyl-terminated polysulphone oligomers are prepared by the condensation of an excess of the alkali metal salt of bisphenol-A with 4,4'-dichlorodiphenylsulphone in anhydrous dimethyl sulphoxide[4]:

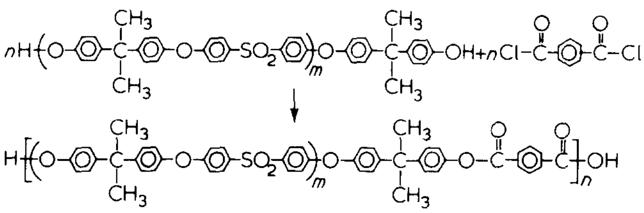


The average degree of polymerization of the oligomer, $\tilde{m}$, can be defined by simple equations[5]:

$$\tilde{m} = \frac{1}{q} \quad \text{and} \quad q = \frac{M_A}{M_B} - 1$$

where, M_A is the number of moles of bisphenol-A and M_B is the number of moles of 4,4'-dichlorodiphenylsulphone: therefore q is the excess number of moles of bisphenol-A. The preparation of some dihydroxyl-terminated polysulphone oligomers are shown in *Table 1*. These oligomers are easily soluble in chloroform, methylene dichloride and other chlorinated hydrocarbon solvents. *Figure 1* is one of the i.r. spectra of the oligomers which reveals an aromatic hydroxyl absorption at 3380 cm^{-1}.

Low temperature solution polycondensation[6] is one of the most successful methods for the preparation of the polysulphone–arylate block copolymers. The dihydroxyl-terminated polysulphone oligomer was dissolved in chloroform and triethylamine was added as the hydrogen chloride acceptor. To the solution were added the corresponding dicarboxylic acid chlorides which were carefully purified before use, the block copolymer was readily obtained:



The structure of the block copolymer in the above equation is, of course, idealized. Because the dihydroxyl-terminated oligomers and the acid chlorides can interact

Table 1 Preparation of dihydroxyl-terminated polysulphone oligomers

No.	M_A/M_B	$\tilde{m}$	Calc. $MW \times 10^{-3}$	Yield (%)	Analysis Calc.	Analysis Found
SM-2	1.50	2	1.113	95	C 74.4 H 5.4	74.0 5.3
SM-3	1.33	3	1.556	97	C 74.1 H 5.3	73.9 5.1
SM-4	1.25	4	1.998	98	C 73.9 H 5.3	73.6 5.1
SM-5	1.20	5	2.441	98	C 73.8 H 5.2	73.5 5.2

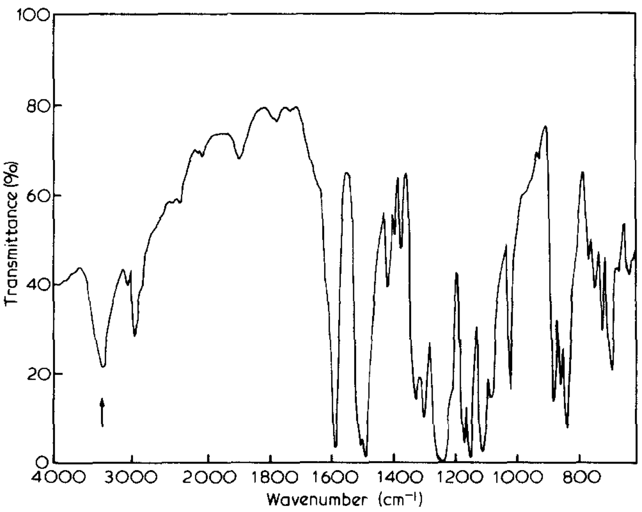


Figure 1 Infra-red spectrum of the oligomer, SM-4 (KBr disc)

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Table 2 Polycondensation of the polysulphone oligomers (SM-4) with iso- and terephathaloyl chloride

No.	Oligomer (mol)	Acid chloride (mol)		Iso-/tere-	Yield (%)	$\eta_{red.}$
		Iso-	Tere-			
PSA-17	0.015	0.015	–	100/0	91	0.49
PSA-18	0.010	0.009	0.001	90/10	91	0.48
PSA-19	0.010	0.007	0.003	70/30	94	0.45
PSA-20	0.015	0.0075	0.0075	50/50	92	0.51
PSA-21	0.010	0.003	0.007	30/70	93	0.47
PSA-22	0.010	0.001	0.009	10/90	93	0.58
PSA-23	0.015	–	0.015	0/100	94	0.49

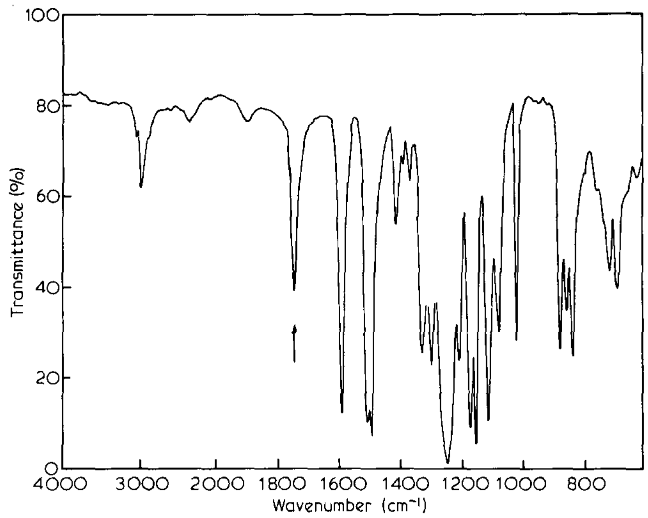

Figure 2 Infra-red spectrum of the block polysulphone–arylate copolymer PSA-22 (film)

with each other and not with themselves, the structures of the block copolymers are strictly controlled. As can be seen from the above equation, the block copolymers have an alternating $\{A_m$–B–R) block sequence sequence structure. The preparation of some block copolymers is shown in *Table 2*. These polymers are soluble in chloroform, dimethyl sulphoxide, *N*,*N*-dimethyl acetamide and *N*-methyl pyrrolidone. Films cast from the chloroform solution of the block copolymers are transparent, colourless, strong and flexible and appear to be homogeneous. According to preliminary tests, the films have good mechanical and electric properties. *Figure 2* shows an i.r. spectrum of a block poly(sulphone–arylate) copolymer, revealing a carbonyl absorption at 1745 cm^{-1} and no absorption in the region of the hydroxyl group.

Experimental

Reagents and general. Bisphenol-A and 4,4′-dichlorodiphenyl sulphone were polymerization grade. Isophathaloyl chloride and terepathaloyl chloride were reaction of the corresponding acid with thionyl chloride and a small quantity of pyridine. The acid chlorides were crystallized carefully from hexane twice or more. Chloroform used in the polycondensation was washed with water, dried over calcium chloride and distilled. Triethylamine was dried over potassium hydroxide and fractionated. The other chemicals were analytical grade.

The reduced viscosities of the block copolymers were measured in chloroform (0.2 g/100 ml) at 25°C. For i.r. spectra the oligomers were used as potassium bromide discs; block copolymers were used as films.

Dihydroxyl-terminated polysulphone oligomers. A typical preparation of an oligomer was as follows. A 1 l five-necked round-bottomed flask was equipped with a nitrogen inlet, mechanical stirrer, thermometer, dropping funnel and a short Vigreux column. Bisphenol-A (142.69 g, 0.625 mol), 500 ml of dimethyl sulphoxide, 100 ml of toluene and potassium hydroxide (70.13 g, 1.25 mol, soluble in 70 ml water) were added. The flask was heated in an oil bath to 130°–140°C and water was removed by azeotropic distillation. When the distillation slowed down, the temperature of the contents was lowered below 100°C, 50 ml of toluene was added through the funnel and the distillation carried out again. This procedure was repeated 3 times, and the temperature of the mixture was raised to 150°–155°C and maintained at this level for 1 h to remove the last traces of water. The heating was stopped. After the temperature of the mixture had fallen to 40°–50°C, 4,4′-dichlorodiphenylsulphone (143.55 g, 0.5 mol) was added, and the reaction temperature raised rapidly again to 145°C and maintained at this level for 6 h. It was then raised to 160° and held for $\frac{1}{2}$ h. After cooling to room temperature, the product was poured slowly with stirring into 2 l water which contained 80 g oxalic acid. The oligomer was kept in this acid solution for 10 h. The filtered product was washed with distilled water. The product (245 g, 98% yield) melted at 145°–160°C and was an off-white powder which contained no chloride as observed by the sodium fusion test.

Polysulphone-arylates. A typical synthesis is as follows. A 250 ml flask was flame dried and fitted with a mechanical stirrer, a thermometer and a drying tube. Oligomer (19.98 g, $\bar{m} = 4$, 0.01 mol) and chloroform (50 ml) were added. The flask was cooled to 10°C and 3 ml of triethylamine was added with stirring. A mixture of isophathaloyl chloride (0.203 g, 0.001 mol) and terephathaloyl chloride (1.827 g, 0.009 mol) was added directly. The temperature of the reaction mixture raised to 22°C immediately and the solution became viscous. The polymerization temperature was held at 18–20°C for 3 h, then the viscous polymer solution was diluted with 200 ml chloroform. The polymer was precipitated by pouring the diluted solution into several volumes of ethanol. The precipitate was washed thoroughly with water and dried at 60°C in vacuum. Alternatively, the dilute polymer solution may also be poured into a big enamel dish and the solvent evaporated to give white polymer film which was then cut to small pieces and boiled with water to remove the triethylamine hydrochloride salts. The yield of the block copolymer was above 90% and the reduced viscosity in chloroform at 25°C was 0.58. Transparent, colourless, strong and flexible films can be cast from the chloroform solution of the block copolymer.

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Influence of roll embossing on polypropylene film

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Roll embossing is an intermediate stage, introduced between melt casting and drawing in a fibre-from-film extrusion line. The unit consists of a pair of temperature-controlled rolls, one of which is grooved circumferentially. The roll embossing process introduces an additional range of technological parameters, the potential of which and the load carrying behaviour of the resulting embossed films are the focus of this communication.

Experimental

The basic test material was a 4.5 *MFI* polypropylene (ICI, GWE27), and the process conditions were: extrusion temperature, 240°C; screw speed 38 rev min^{-1}; take-up speed 17 m min^{-1}; chill roll temperature 10°C; embossing roll width 500 mm; groove pitch 33 grooves cm^{-1}; groove depth 200 μm; roll speed 17 m min^{-1}.

Films were produced in 100, 150 and 225 μm thicknesses and subsequently embossed at roll temperatures between 70–105°C and at roll pressures between 2–10 MPa.

Material structure variations were identified using small-angle light scattering (SALS), small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS)[1].

Static and dynamic mechanical properties were determined using an Instron Universal Test Machine and a sonic apparatus[2].

Results

An increase in the thickness of as-cast film resulted in a greater degree of crystallinity (as indicated by density measurements, *Figure 1*), enhanced crystalline order and larger spherulite size (*Figures 2* and *3*), all resulting as expected, from a less effective quench as film thickness increases.

For 100 and 150 μm thick films–provided the temperature of the embossing roll was at least 90°C — both the amount of crystallinity and the order and size within the crystallites (as evidenced by monoclinic formation and sharpening of the diffraction rings) was greater than in the corresponding as-cast films. No such changes could occur in the 225 μm film, this already having an orderly crystalline structure.

Embossing caused some longitudinal crystalline orientation in 100 μm thick films (as indicated by WAXS and SAXS patterns, *Figure 2*). 150 μm thick film underwent some longitudinal spherulitic deformation and showed both longitudinal and transverse cyrstalline orientation. The 225 μm film showed a considerable longitudinal spherulitic orientation (as indicated by SALS patterns, *Figure 3*) but without any crystalline orientation, over the entire temperature and pressure range. The presence of some overall orientation in all samples was also demonstrated by an increase in sonic modulus.

Tenacity, yield strength and sonic modulus values were all found to increase with increasing embossing temperature or pressure; this increase being more pronounced with 100 and 150 μm thick films. Longitudinal elongation at break did not alter for 100 and 150 μm films but increased for 225 μm film. Transverse elongation was reduced for all but the 225 μm film.

Discussion

Roll embossing has been shown to improve the tenactiy of the final drawn tape by as much as 15%[3], and the aim of this work was to identify the mechanism through which this improvement is achieved. The increase in mechanical strength of embossed films is considered to result from improved crystalline structure and longitudinal orientation, particularly crystalline orientation. Under the same draw process conditions, the embossed film will achieve a greater degree of nett orientation[4] compared with non-embossed film, hence exhibiting greater tenacity.

A further contributory factor of the increased tenacity

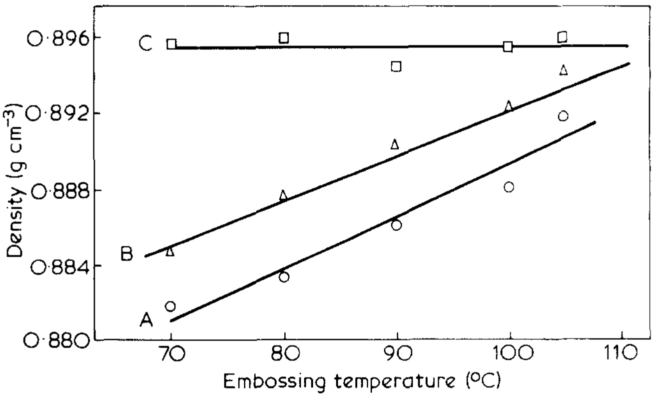

Figure 1 Density vs. embossing temperature for film thicknesses, A, 100 μm; B, 150 μm; C, 225 μm

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