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THE THERMAL PROPERTIES AND SOLVENT STRESS CRACKING RESISTANCE OF SOME NEW POLYETHERS

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ABSTRACT

The thermal properties and solvent stress cracking resistance of some polyethers synthesized from 2,2-bis-(4-chlorophenyl)-1,1,1-trichloroethane (I) or its derivatives, and 2,2-bis(4-hydroxyphenyl)-propane(II) are reported, i.e. decomposition temperature, activation energy, softening point, fracture time, etc. The effect of molecular weight on the thermal stability and glass transition temperature of polysulphones is included. The properties of the copolymers prepared from the derivatives of (I) and bis(4-chlorophenyl)sulphone(III) were also studied The copolymers have better resistance toward cracking solvents than polysulphone.

INTRODUCTION

During an earlier programme of research [1,2] a number of new synthetic polymers and copolymers were synthesized by polymerizing each of the following monomers with 2,2-bis(4-hydroxyphenyl)-propane (II): 2,2-bis(4-chlorophenyl)1,1,1-trichloroethane (I), 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (IV), 2,2-bis(3-nitro-4-chlorophenyl)-1,1,1-trichloroethane (V), and 2,2-bis(3-nitro-4-chlorophenyl)-1,1-dichloroethylene (VI).

In this paper, some of the thermal properties and solvent stress cracking resistance are reported.

EXPERIMENTAL

Polymer preparation

The homopolymers were prepared by condensation of each of I, IV, V and VI with II in the presence of NaOH in dimethylsulphoxide solution. The copolymers were prepared by polymerizing different molar ratios of III/V or VI with II.

Polysulphones of different molecular weights were prepared by varying the polymerization time, following the procedure used by Johnson [3,4].

The polymers were characterized, and their characteristics are listed in Table 1.

Softening point

The softening point of these polymers was determined using a Kofler Hot Bench type 184321. The instrument was calibrated with pure standard materials.

From the instantaneous slopes of the curves in Fig. 2 at different temperatures, the energy of activation of the decomposition process over the initial 10% weight loss was calculated. The results obtained are shown in Table 1.

Molecular weight

The number average molecular weights, $\bar{M}_n$, were measured in chloroform solution at 32°C with a Hitachi Perkin—Elmer vapour pressure osmometer model 115. The limiting viscosity number was found from the relative viscosity measurements in chloroform solutions using a Ubelohde viscometer at 25 ± 0.01°C.

TABLE 1

Properties of the polymers refered to in this paper

	Type of polymer	$\bar{M}_n \times 10^{-3}$ (VPO)	$[\eta]$ (cm^3 g^{-1})	Softening temp. (T_s) (°C)	Decomposition temp. (DTG) (°C)	Activation energy, E (kJ mole^{-1}
1	Polysulphone	5	18	135	420	70 ± 5
2	Polysulphone	12	40	140	460	90 ± 10
3	Polysulphone	20	73	175	470	120 ± 15
4	Polysulphone	30	106	190	490	130 ± 20
5	Polysulphone	36 ± 6 [a]	117	190	490	130 ± 20
6	Polysulphone	45 ± 15 [a]	130	200	510	145 ± 25
7	Poly (I—Co—II)	1.5	3.7	108	420	88 ± 10
8	Poly (IV—Co—II)	2.4	6.4		430	90 ± 10
9	Poly (V—Co—II)	2.7	6.9	140	315	45 ± 5
10	Poly (VI—Co—II)	7.1	19.8	203	325	55 ± 5
11	5% V copolymer	5.6	17.4	198	380	75 ± 5
12	10% V copolymer	6.7	18.2	195	440	80 ± 10
13	25% V copolymer	4.2	11.2	185	385	65 ± 5
14	50% V copolymer	4.4	11.5	178	350	70 ± 5
15	5% VI copolymer	9.8	27.2	215	390	80 ± 10
16	10% VI copolymer	11.0	30.2	225	415	85 ± 10
17	25% VI copolymer	15.3	49.1	230	400	90 ± 10
18	50% VI copolymer	12.6	39.3	250	375	85 ± 10

[a] These values are outside the accurate range of the instrument used.

Thermal analysis

Thermogravimetry was carried out using a Perkin—Elmer thermobalance TGS-1 and a MOM derivatograph, both instruments were calibrated before use. The TGS-1 was used for the isothermal study of polymers and also to measure the weight loss vs. temperature. The derivatograph was used to measure the TG, DTG and DTA simultaneously vs. temperature at a heating rate of 10°C min^{-1} in the presence of air.

The solvent stress cracking resistance

For this test, 1 mm films were cast from 15% polymer solutions in chloroform and dried at room temperature for 24 h and then under vacuum at 65°C for 8 h. Specimens of length 50 mm and width 5 mm were cut from these films.

The polymeric strips were subjected to a constant bending stress, as shown in Fig. 1, and the bent specimen placed in a beaker containing the organic solvent. The times required to the crack formation and fracture time were recorded. Ten specimens were used in each test. The effect of several organic solvents was examined on the polysulphones and our new products.

RESULTS AND DISCUSSION

Thermogravimetric measurements

This technique measures the weight loss of the polymer sample either by keeping the polymer at a constant temperature and observing the weight loss as a function of time, or by raising the temperature at a steady rate (10°C min^{-1}) until the polymer is substantially decomposed (Fig. 2).

The results showed that molecular weight strongly affected the thermal stability of polysulphone. The results showing the effect of molecular weight

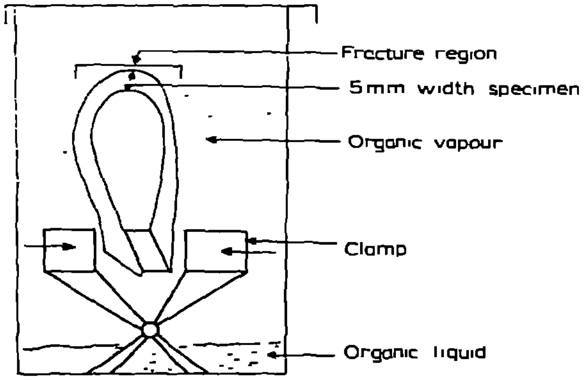

Fig. 1. The technique used for measuring the solvent stress cracking resistance in the presence of organic vapours.

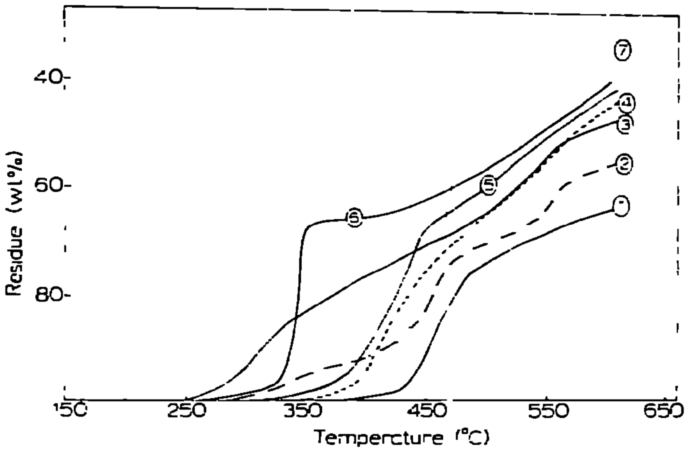

Fig. 2. Weight loss by thermal decomposition of different polyethers and copolymers at a steadily increasing temperature. (1) Polysulphone ($\overline{M}_n$ = 12 000); (2) 10% VI copolymer; (3) poly(V—Co—II); (4) poly(IV—Xo—II); (5) poly(I—Co—II); (6) poly(VI—Co—II), (7) 10% V copolymer.

on the initial isothermal weight loss at 400° C are given in Fig. 3, which also shows that the amount of decomposition is much greater with low molecular weight polysulphone. This is probably due to the number of phenolic chain ends, similar to poly[2,2-propane-bis(4-phenyl)carbonate] [5].

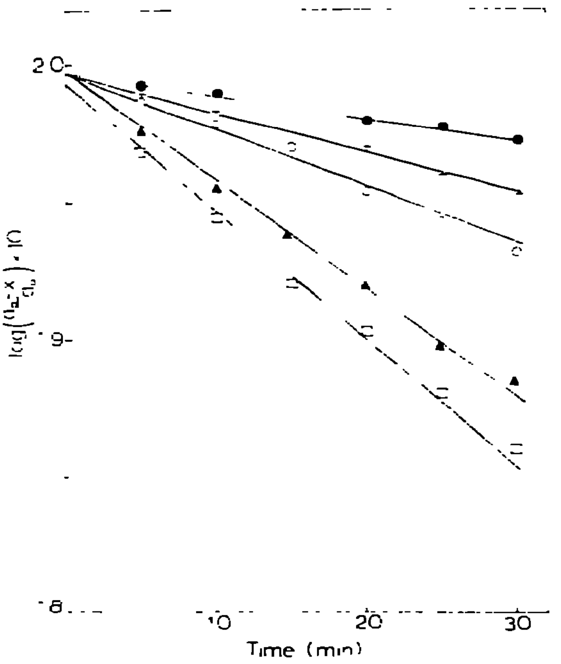

Fig. 3. Effect of molecular weight on the isothermal decomposition of polysulphones. ●, $\overline{M}_n$ = 45 000, ×, $\overline{M}_n$ = 30 000; ⊙, $\overline{M}_n$ = 20 000; ▲, $\overline{M}_n$ = 12 000; ⊡, $\overline{M}_n$ = 5000; where a_0 is the initial weight and x is the weight loss.

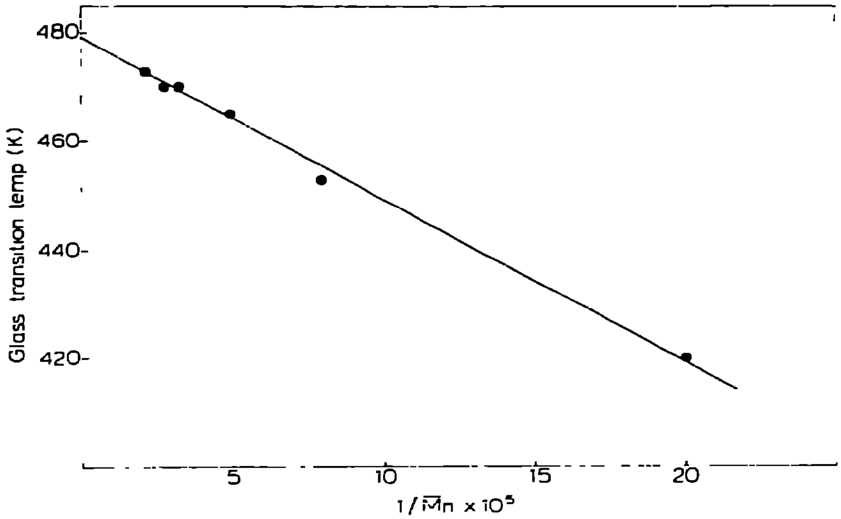

Fig. 4. Effect of molecular weight on the glass transition temperature of polysulphone.

Differential thermal analysis measurements (DTA)

The glass transition temperature, T_g, may be readily estimated by DTA making use of the marked change in the specific heat which occurs at T_g. The molecular weight exerts a great effect on the T_g of polysulphones. The results (see Fig. 4) followed the conventional type of relationship between T_g and $\bar{M}_n$ [6,7] so that

$$T_g = T_g^{\infty} - A M_n^{-1}$$

where $T_g^{\infty} = 479$ K and $A = 3 \times 10^5$ mole K.

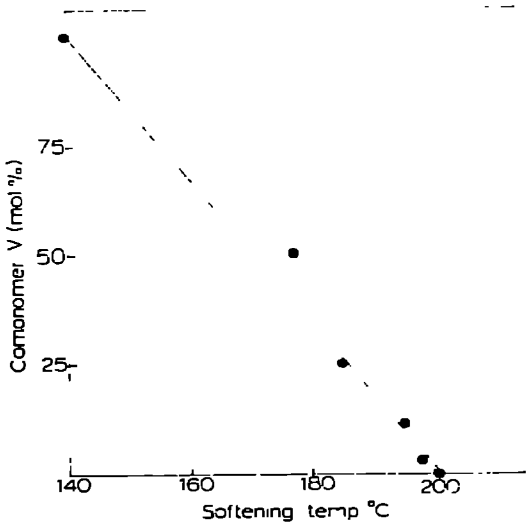

Fig. 5. Effect of copolymerization on the softening temperature of the polymers.

TABLE 2

The solvent stress cracking resistance as a function of fracture time measured in the presence of organic solvent vapour at 25°C

Organic liquid [a]	Fracture time (min)		
	Polysulphone	10% V copolymer [b]	10% VI copolymer
Methanol (z)	1.16 ± 0.25	60	60
Ethanol (z)	1.33 ± 0.25	60	60
Acetone/water (50/50)	0.67 ± 0.05	30	30
Carbon tetrachloride (k)	2.35 ± 0.33	8.5 ± 1	7.5 ± 1
Methyl acetate (k)	2 ± 0.33	14 ± 1.25	12 ± 1.25
Methyl butyl ketone (k)	1.67 ± 0.25	11.5 ± 1	11 ± 1

[a] z = Crazing agent, k = cracking agent.
[b] Percentage of comonomer V in the copolymer.

Another feature which was observed in this study was the decrease in the softening temperature (T_s) with increase in the amount of comonomer(V) in the copolymer (Fig. 5), while T_s increases with increasing amounts of the comonomer(VI) (see Table 1).

Solvent stress cracking resistance

The fracture time for the copolymer specimens was relatively longer than for the polysulphone specimens of similar molecular weights (see Table 2).

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