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CALORIMETRIC INVESTIGATIONS OF GLASS TRANSITIONS AND PHASE SYSTEMS OF POLY(ARYLATE-ARYLENESULFONE OXIDE) BLOCK COPOLYMERS

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ABSTRACT

Statistical poly(arylate-arylenesulfone oxide) block copolymers derived from phenolphtalein, terephthaloyl chloride and polyarylene sulfone oxide with degree of polymerisation, DP:10, DP:30 and DP:100 were investigated by DSC-2. The investigations were carried out on the systems containing from 0.5% to 90% arylenesulfone oxide.

The aim of this work is to study the influence of degree of polymerisation of arylenesulfone oxide on the phase behaviour of the block copolymer.

The results indicate that in the case of DP:10 there was a single phase system with a single glass transition temperature, which follows the commonly used T_g-composition relations. For all compositions the block copolymers with DP:30 and DP:100 showed a multiphase behaviour with two glass transition regions.

INTRODUCTION

There is no doubt that the connection of polymeric segments of different types into block copolymers may be at the present time the most promising method of obtaining polymers with unusual and valuable combinations of properties.

One of the characteristic features of block copolymers is the tendency for microphase separation to occur in the solid state. The morphology of such multiphase systems influences their behaviour and can be controlled by altering the length of blocks and their ratio.

Thermostable block copolymers based on structurally similar homopolymers with high glass transition temperatures including, polyarylate-arylenesulfone oxide block copolymers, (ϕ-2)-(PASO), have for some time been the subject of complex preparation, process and property investigations by V.V.Korshak et al. (ref.1). In this work, differential scanning calorimetry was used to study phase behaviour in the system (ϕ-2)-(PASO).

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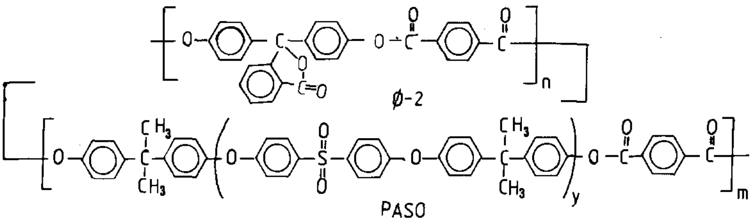

ϕ-2

PASO

EXPERIMENTAL

Materials. Series of statistical (ϕ-2)-(PASO) block copolymers derived from phenolphthalein, terephthaloyl chloride and polyarylene sulfone oxide with degree of polymerisation, DP:10, DP:30 and DP:100 (Series ϕ-2-10-x, ϕ-2-30-x and ϕ-2-100-x, respectively) were prepared by a low temperature polycondensation method in Moscow by I.P.Storozhuk (ref.1). In all series the content of polyarylenesulfone oxide (x) varied over the weight-% range of 0.5 to 90.

Differential Scanning Calorimetry Measurements. The glass transition temperatures T_g and heat capacities were measured using a Perkin Elmer DSC-2 connected with an Apple II microcomputer.

The temperature scale was calibrated with metal standards at 10 K/min heating rate. In the heat capacity measurements a 29.540 mg saphire disc was used for the calibration of the enthalpy scale. All measurements were made at a heating rate 10 K/min over the temperature range 323-623 K. In order to obtain a more repeatable transition behaviour all samples were first scanned at a rate 80 K/min over the temperature ranges 323-623 K and 623-323 K.

The measurements were carried out on 10 mg (dia 4,5 mm) pellets formed under pressure.

RESULTS AND DISCUSSION

Series ϕ-2-10-x exhibit a single, composition dependent glass transition by DSC as has been shown by the methods of dipole polarisation, thermostimulated depolarisation currents, electroconductivity and in the results of thermomechanical investigations (ref.2).
The experimental dependence of T_g on composition follows a number of T_g-composition relations including Fox (1), Gordon (2) and Fried (3) (ref.3,4,5).

$$(1/T_g) = (w_1/T_{g1}) + (w_2\ /T_{g2}) \qquad (1)$$

$$T_g = (w_1T_{g1} + w_2T_{g2}k)\ /\ (w_1 + k\ w_2) \qquad (2)$$

$$\ln(T_g/T_{g1}) = w_2\ln(T_{g2}/T_{g1})\ /\left[(w_1(T_{g2}/T_{g1}) + w_2\right] \qquad (3)$$

T is the glass transition temperature of the system, T_{g1} and T_{g2} glass transition temperatures of homopolymers and w_1 and w_2 the weight fractions,respectively; k is an empirical parameter, here $k=\Delta cp2/\Delta cp1=2{,}4095$

The values calculated accordingly are compared in table 1 with the T_g found experimentally. Calculated values are satisfactorily close to the experimental temperatures, particularly $T_g(2)$, which indicates a total phase mixing (see Fig. 1a).

TABLE 1

Experimental and calculated glass transition temperatures of series ϕ-2-10-x

x (%)	Experimental	Calculated		
	T_g(K)	$T_g(1)$	$T_g(2)$	$T_g(3)$
0 (0-2)	591	-	-	-
5	524	580	573	579
10	512	570	557	567
20	505	550	531	545
50	478	499	478	492
70	458	469	455	465
90	445	443	438	441
100 (PASO)	431	-	-	-

$T_g(1)$, $T_g(2)$ and $T_g(3)$ calculated in accordance with equations (1)(2) and (3).

Series ϕ-2-30-x and ϕ-2-100-x showed for all compositions a multiphase behaviour with two distinct T_gs.

Glass transitions occur within wide overlapping temperature intervals which complicates the analyzing of specific heat jumps and makes it impractical to calculate the degree of phase mixing.

Up to 10% content of (PASO) blocks, in series 0-2-30-x, the T_g of (ϕ-2) phase decreases drastically, then on, it remains practically unchanged, whereas the T_g of (PASO) increases slightly; this is evidence of an incomplete phase separation (see Fig.1b).

With DP:100 (series ϕ-2-100-x) T_g of the (ϕ-2) phase also decreases drastically reaching a minimum with 10% content of (PASO) blocks and then increases again to that of the initial homopolymer, whereas the PASO phase remains unchanged at any composition (see Fig. 1c). This indicates the isolation of (ϕ-2) blocks as a separate phase. Nevertheless the decrease in the glass transition temperatures of the (ϕ-2) confirms the occurence of interaction between the phases. In all series (PASO) acts as a plasticizer on the (ϕ-2) matrix.

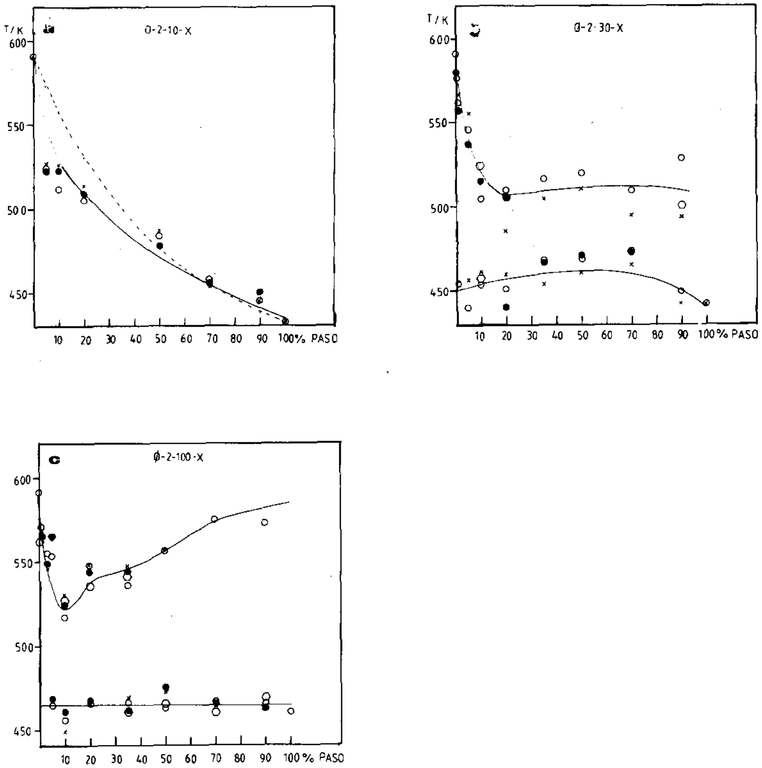

Fig. 1. Dependence of glass transition temperatures for (ϕ-2)-(PASO) block copolymers on the PASO content. (a) DP of PASO blocks is 10; experimental values (solid line) and teoretical values calculated according to eq. (2) (broken line). (b) DP of PASO blocks is 30. (c) DP of PASO blocks is 100.

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