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Rigid Backbone Polymers

Effects of Width of Chain-Length Distribution on the Phase Behavior of Poly(n-Octyl Isocyanate)

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SUMMARY.

Coexisting isotropic and anisotropic solutions of poly(n-octyl isocyanate)s (POIC) were prepared from parent polymers of increasing width of molecular weight distribution. In qualitative agreement with theoretical predictions, analysis of the coexisting phases indicates the efficiency of partitioning into said phases to increase with increased width of the distribution in the parent polymer.

INTRODUCTION.

In recent years there appeared in the literature several studies relating the molecular weight distribution of a parent polydisperse rodlike polymer, and the width of this distribution, to the partitioning of said polymer into coexisting isotropic and anisotropic solutions. FLORY and FROST analyzed the most probable (1978a) and Poisson (1978b) distributions while MOSCICKI and WILLIAMS (1981,1982a,1982b) considered the Gaussian distribution. In this communication, preliminary results pertaining to the relationship between the width of the molecular weight distribution of the parent polymer and its partitioning among the coexisting phases, are presented.

EXPERIMENTAL.

The liquid crystalline polymer investigated in this work, poly(n-octyl isocyanate)(POIC), was synthesized as described in detail previously (AHARONI 1979). Since POIC is anionically polymerized under conditions identical to poly(n-alkyl isocyanate)s previously characterized by us (AHARONI 1979, AHARONI and WALSH 1979a,1979b), the ratio of weight average to number average molecular weight in the synthesized polymer, M^o_w/M^o_n, is estimated to be 1.4±0.1, close to the other poly(n-alkyl isocyanate)s (AHARONI 1979, AHARONI and WALSH 1979a,1979b). All M_w^o values were calculated according to BUR and FETTERS (1973) from intrinsic viscosities of toluene solutions obtained in Cannon-Ubbelohde internal dilution glass viscometers at 25°C. All biphasic solutions of POIC were obtained in toluene. The systems were prepared in graduated tubes and maintained at 30°C throughout. The solvent was added, with initial stirring, to the solid polymer and after the phases started to separate into two layers, the amount of solvent was adjusted in such a way that when equilibrium was finally reached, about 55 to 60% of the total volume was anisotropic with the rest of the volume being isotropic. A period of not less than one month was required for the equilibrium to be established. Once settled, the two phases were carefully separated, and the weight average molecular weight in the isotropic, M_w, and in the anisotropic, M_w', phases determined from intrinsic viscosity measurements of the polymer retrieved from each solution.

RESULTS AND DISCUSSION.

The three parent POICs used in this study had intrinsic viscosity values of 0.31, 0.92 and 1.28 dL/g, corresponding to M_w^o = 39000, 67200 and 79300(BUR and FETTERS 1973), respectively. Concentrations of about 43-45 wt/vol % of the lowest M_w^o polymer in toluene were needed for anisotropy to appear, decreasing to less than 20% concentration for the highest M_w^o polymer Thus, data from fractionation of the POIC with M_w^o = 39000 were not obtained because of the very high polymer concentration (and the necessary large quantities) needed to reach 55-60% by volume anisotropic phase.

To broaden the molecular weight distribution width, POICs were mixed in ratios indicated in Table I, and then dissolved in toluene in the manner described in the Experimental section. The average molecular weight of the resulting parent polymer, M_w^*, was obtained by linear addition of the molecular weights of the components, properly weighted. For polymers having Gaussian distribution of molecular weight and a more or less constant value of $M_w^o/M_n^o \cong 1.4$, $W_{\frac{1}{2}}$ the half width of the distribution is, of necessity, a function of M_w^o. Thus, in a graphic description of the Gaussian distribution of the volume ratio of species of size x, V_x, to all polymeric species, V_p, the peak of the curve becomes smaller in magnitude and the curve itself broadens, as it shifts to higher and higher average molecular weight. Using this approach of MOSCICKI and WILLIAMS (1982a) in their "calculation

C", and approximating the Gaussian peak positions by the M_w^o of the parent POICs, we were able to obtain, at least qualitative, estimates of the overall shapes and widths of the M_w^* molecular weight distributions of the polymer mixtures I, II and III, described in Table I.

TABLE I.

Ingredients and Products of POIC Fractionation.

Mol. Wt. & Ratio of polymer in initial solution.	M_w^*	$W_{\frac{1}{2}}/M_w^*$	M_w'	M_w	M_w'/M_w
1) POIC 67200	67200	0.667	70000	56000	1.25
2) POIC 79300	79300	0.667	86500	77400	1.12
3) 1:1 POIC 67200 + POIC 79300 (I).	73250	0.683	86100	65200	1.32
4) 1:1 POIC 39000 + POIC 79300 (II).	59150	1.285	79300	42600	1.86
5) 1:1:1 POIC 39000 + POIC 67200 + POIC 79300 (III).	61830	1.100	62700	43200	1.45

The distributions are shown in Fig. 1, and their $W_{\frac{1}{2}}$ values, measured along the horizontal line at half the height of their M_w^* value, are collected in Table I Notice that the numerical values of the V_x/V_p axis are correct only for M_w^o and should be normalized to be correct for the cumulative M_w^*s.

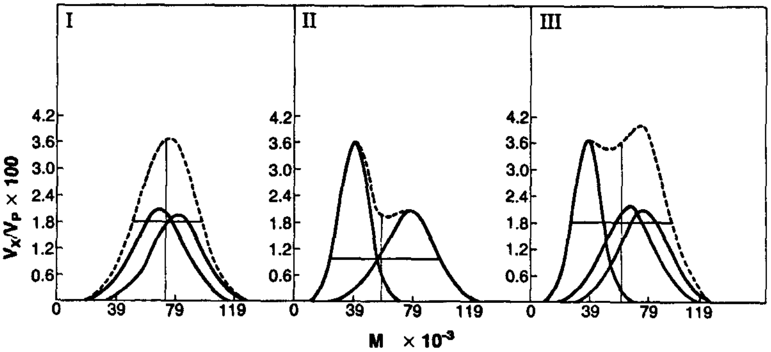

Fig. 1. Molecular weight distribution in parent mixtures, assuming Gaussian distribution in M_w^o.

It is important to realize that the ratios W_1/M_w^* may not be precise, but since the last three entries in Table I were calculated on the basis of the first two entries, the trend of M_w'/M_w as function of W_1/M_w^* in the Table is clear and, at least qualitatively, correct.

One may conclude, then, that independently of the exact shape of the molecular weight distribution, it is obvious that the broader the distribution the more efficient the partitioning according to molecular weight between coexisting isotropic and anisotropic solutions and the larger the ratio of M_w' to M_w of the polymer in the two phases. This is in qualitative agreement with the theoretical predictions of FLORY and FROST (1978a,1978b), MOSCICKI and WILLIAMS (1981, 1982a,1982b) and MATHESON (1982).

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