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Physical Properties

Unperturbed dimensions of poly(cyclohexyl methacrylate) and their temperature coefficient

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SUMMARY

Unperturbed dimensions of poly(cyclohexyl methacrylate) and their temperature coefficient were studied. The influence of the character of solvent on the solubility of poly(cyclohexyl methacrylate) are discussed.

The characterization of poly(cyclohexyl methacrylate) in solution was mainly carried out in thermodynamically good solvents. A systematic study in Θ-solvents is missing (1-4). For this polymer, two series of chemically similar Θ-solvents have been found (5), namely, n-alkanes and n-alcohols. It is assumed that the measurements using members of a homologous series of Θ-solvents can eliminate (or appreciably reduce) the so-called solvent effect (6) on the temperature coefficient of unperturbed dimensions.

The original atactic sample of poly(cyclohexyl methacrylate) was obtained from the Röhm Co., Darmstadt, FRG and was divided into fractions by the precipitational fractionation (M_w/M_n lower than 1.3). Details of the experiments and results have been published elsewhere (5).

For the determination of the unperturbed dimensions, expressed by the K_Θ values of the Mark-Houwink equation in solvent, the same method was applied (7) as in the case of poly(n-butyl methacrylate). The exponents of the Mark-Houwink relation a_Θ, were determined by the least-squares method for several temperatures in the vicinity of the Θ-point and they turned out to be linearly related to the temperature within the temperature range investigated (Fig. 1). The K_Θ values were then calculated as arithmetic means of $[\eta]/M^{0.5}_\Theta$ values established for at least four fractions of widely different molecular weights. The results are summarized in Table 1. Table 1 shows that the Θ-temperature in n-alkanes monotonously

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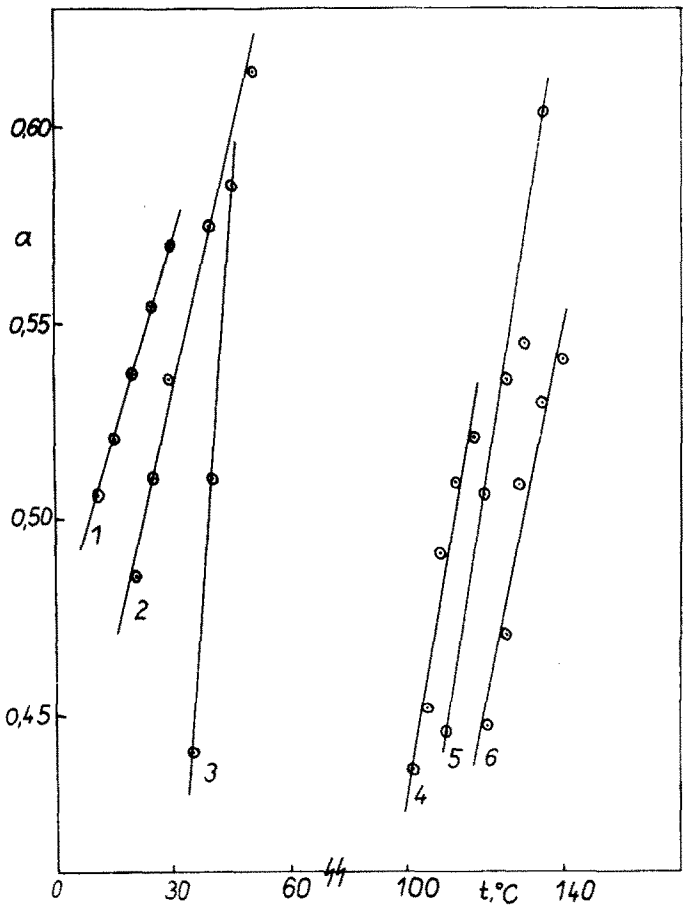

Fig. 1 Temperature dependence of the exponent a of the Mark-Houwink equation: (1) poly(cyclohexyl methacrylate) in n-hexanol, (2) n-butanol, (3) n-propanol, (4) n-octane, (5) n-decane, (6) n-dodecane

increases with molecular weight of the solvents, but n-alcohols exhibit interesting anomaly. The highest temperature is in n-propanol; then Θ-temperature decreases and reaches its minimum in n-hexanol. Further increase of the number of C atoms in the solvent causes a new rise of the Θ-temperature.

This phenomenon is probably connected with the influence of the OH group on the poly(cyclohexyl methacrylate) solubility. In alcohols with shorter alkyl chains this effect is pronounced and the miscibility with the polymer of medium polarity is limited.

Table 1 Θ-temperature and K_o values for poly(cyclohexyl methacrylate)[o] studied

Solvent	Θ (°C)	$K_o x 10^4$	$S x 10^4$ a)
n-propanol	39.2	4.88	0.04
n-butanol	22.7	4.58	0.04
n-hexanol	9.2	4.37	0.03
n-ocanol	17.0	4.51	0.04
n-nonanol	19.8	4.56	0.05
n-decanol	23.0	4.66	0.05
n-octane	112.1	4.08	0.06
n-decane	120.0	4.18	0.05
n-dodecane	129.9	4.36	0.02

a) Standard deviation of K_o values

When the solvent chain is lengthened, the influence of the OH group is weakened and the solubility of the polymer in n-alcohols increases. The highest solubility is in n-hexanol. In alcohols with longer alkyl chains this influence prevails, the polymer solubility is worsened and reflected in the increase of the Θ-temperature.

The unperturbed dimensions increase in all cases as the temperature is raised. The temperature coefficient of unperturbed dimensions, $d\ln R_o^2/dT = 2/3\ d\ln K_o/dT$, was obtained graphically from the established values of K_o (Fig. 1). In both homologous series positive and practically the same values ($2.5 x 10^{-3}\ K^{-1}$ for n-alkanes and $2.6 x 10^{-3}\ K^{-1}$ for n-alcohols) were obtained.

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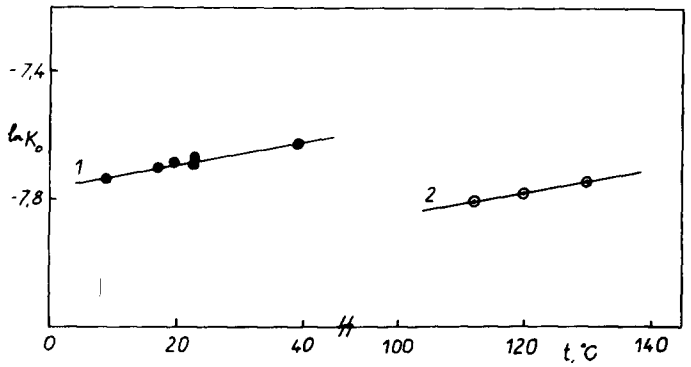

Fig. 2 Temperature dependence of the K_θ values: (1) poly(cyclohexyl methacrylate) in n-alcohols, (2) n-alkanes

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