Solution properties of poly(n-hexyl methacrylate) in homologous series of n-alkanes

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Summary

Dilute solutions of poly(n–hexyl methacrylate) have been studied in the homologous series of alkanes at different temperatures using viscometry. Mark–Houwink relations in solvents widely differing in their thermodynamical quality were established together with the unperturbed dimensions and their temperature coefficient.

Introduction

The literature contains numerous publications on the solution properties of polymethacrylic esters [1], especially of poly(methyl methacrylate) [2] but only little on the solution properties of poly(n-hexyl methacrylate) (PHMA) both in good and θ-solvents [3].
Viscometric method through the knowledge of Mark-Houwink equation, gives the simplest way of molecular weight determination for polymer samples and the application of the homologous series of solvents can eliminate (or essentially reduce the solvent effect on unperturbed dimensions, being present when measurements in chemically dissimilar solvents are performed. This is especially important for determinations of the temperature coefficient of unperturbed dimensions
d ln $\overline{r}_0^2$/dT , where the application of the homologous series of θ-solvents gives the best results.
n-Alkanes were found as such a homologous series of solvents for poly(n-hexyl methacrylate) and the determined temperature dependence of intrinsic viscosity was exploited for characterization of this polymer in solvents widely differing in their thermodynamical quality and at the same time for the determination of unperturbed dimensions, their temperature coefficient and chain flexibility.

Experimental section

Linear poly(n-hexyl methacrylate) was prepared by polymerization of n-hexyl methacrylate (Polysciences Europe GmbH, Eppelheim, Germany) in toluene using azobisisobutyronitrile as initiator at the conditions where substitution reactions of all free radicals with the polymer formed are negligible.
Polymer was fractionated by the method of fractional precipitation, combined with the lowering of temperature from 30 °C to room temperature by using solvent-nonsolvent

system: acetone-ethanol [3]. All fractions were characterized viscometrically in tetrahydrofuran at 30 °C and selected ones by light scattering (Brookhaven BI-200 SM goniometer, butanone or n-octane, 25 °C) and by membrane osmometry (Hewlett-Packard automatic osmometer, toluene, 37 °C). From these measurements Mark-Houwink equation $[\eta] = 1.94 \times 10^{-5} M^{0.76}$, THF, 30 °C was established. Molecular weights of polydisperse sample and fractions with their distributions of molecular weight were determined by gel permeation chromatography using universal calibration. Only fractions with polydispersity $M_w/M_n = 1.2$ and less were used in the study of solution properties.

The solution viscosities were measured in Ubbelohde dilution viscometers and intrinsic viscosities were determined using the Huggins equation.

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \qquad (1)$$

where $[\eta]$ is intrinsic viscosity, k_H Huggins constant and c concentration

The polymer solutions were prepared within the concentration range from 0.1 to 0.8 gdl^{-1} and temperature control during the measurements was ±0.05 °C.

Typical plots of η_{sp}/c versus c for the data obtained in the solvent system are given in Fig.1; values obtained for intrinsic viscosity are summarized in Table1.
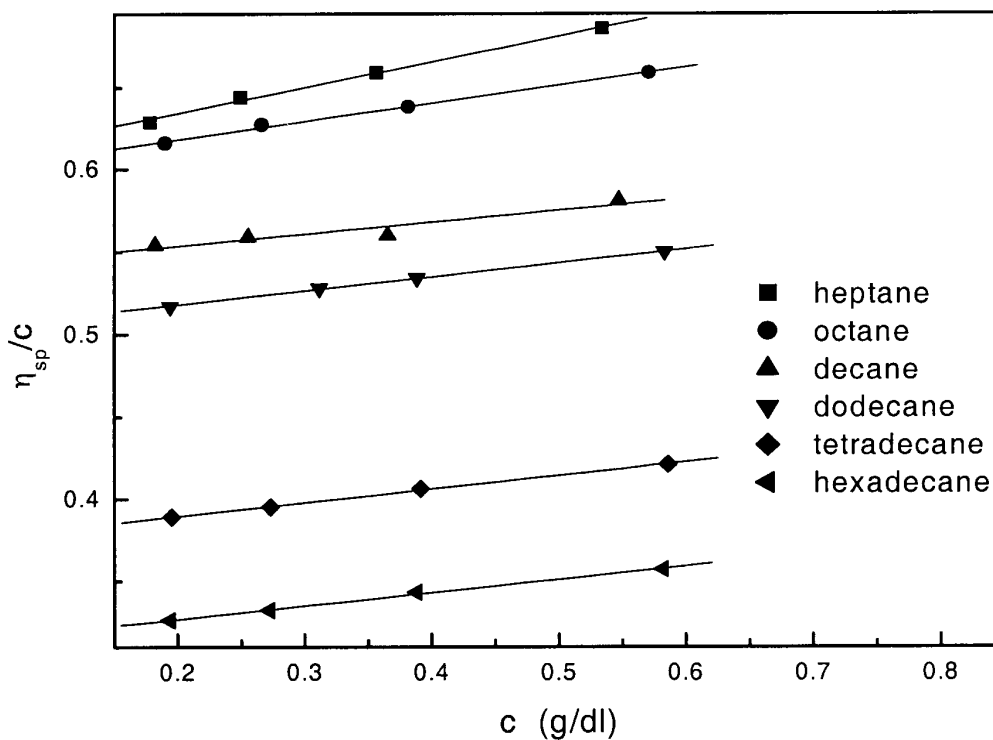
Figure 1 Relation between reduced viscosity and concentration for PHMA ($M_w = 569 \times 10^3$) in n–alkanes at 60 °C.

Table 1 Intrinsic viscosity of PHMA fractions in n–alkanes at different temperatures

n-alkanes	$M_w 10^{-3}$	$[\eta]$ dl/g at			
		30 °C	40 °C	50 °C	60 °C
heptane	569	0.49_1	0.54_8	0.57_1	0.57_4
	493	0.44_1	0.49_0	0.51_4	0.52_4
	438	0.40_0	0.44_5	0.46_6	0.47_0
	248	0.28_0	0.30_8	0.32_0	0.32_3
octane	569	0.46_0	0.50_3	0.54_7	0.59_0
	493	0.41_5	0.45_9	0.48_8	0.52_9
	438	0.37_8	0.41_8	0.44_2	0.48_7
	248	0.26_4	0.28_7	0.30_7	0.32_7
decane	569	0.39_3	0.45_3	0.50_6	0.53_6
	493	0.36_4	0.40_3	0.44_0	0.48_0
	438	0.33_7	0.37_8	0.41_8	0.45_0
	280	0.25_8	0.29_0	0.31_9	0.33_8
dodecane	569	0.29_4	0.35_9	0.40_5	0.50_0
	493	0.27_2	0.33_3	0.37_3	0.46_0
	438	0.25_4	0.31_0	0.34_7	0.42_0
	280	0.19_8	0.23_9	0.26_6	0.31_9

n-alkanes	$M_w 10^{-3}$	35 °C	40 °C	50 °C	60 °C	70 °C
tetradecane	569	0.24_1	0.27_0	0.32_6	0.37_3	0.44_8
	493	0.22_8	0.24_2	0.28_9	0.35_7	0.42_2
	438	0.21_4	0.21_8	0.26_9	0.33_8	0.39_7
	248	0.16_2	0.17_3	0.20_4	0.23_4	0.27_0

| n-alkanes	$M_w 10^{-3}$	50 °C	55 °C	60 °C	70 °C	80 °C
hexadecane	569	0.24_6	0.27_5	0.31_0	0.37_0	0.48_2
	493	0.23_4	0.25_8	0.27_8	0.35_2	0.40_9
	438	0.22_3	0.24_5	0.26_3	0.33_3	0.38_2
	280	0.17_3	0.19_0	0.20_7	0.24_8	0.29_7

Results and discussion

The applied homologous series of n-alkanes enables the viscometric characterization of PMMA in solvents widely differing in their thermodynamical quality. The intrinsic viscosity and molecular weight data (Table 1) yield the Mark-Houwink relationships $[\eta] = KM^a$ under both ideal and nonideal conditions, the parameters of which are presented in Table 2. These results show that the solubility of PHMA in n-alkanes increases with solvent chain length decrease and temperature increase.

Table 2 Parameters a, and K of Mark–Houwink equation for PHMA in n–alkanes

| n-alkanes	a	$K \times 10^4$	a	$K \times 10^4$	a	$K \times 10^4$	a	$K \times 10^4$	a	$K \times 10^4$
	30 °C		40 °C		50 °C		60 °C			
heptane	0.67	0.70	0.68	0.63	0.69	0.58	0.69	0.59	–	–
octane	0.66	0.72	0.68	0.64	0.69	0.62	0.71	0.50	–	–
decane	0.59	1.36	0.61	1.32	0.62	1.29	0.65	1.02	–	–
dodecane	0.55	1.91	0.57	1.81	0.59	1.58	0.63	1.05	–	–
	35 °C		40 °C		50 °C		60 °C		70 °C	
tetradecane	0.49	3.77	0.51	2.89	0.54	2.44	0.58	1.85	0.62	1.24
	50 °C		55 °C		60 °C		70 °C		80°C	
Hexadecane	0.49	3.56	0.51	3.08	0.54	2.42	0.57	1.97	0.63	1.10

The comparison with the same measurements on poly(n–butyl methacrylate) [4] shows that the small change of the side chain length dramatically improves the solubility of PHMA in n-alkanes, the same is valid for the comparison with poly(cyclohexyl methacrylate) [5], where the polymer with linear side chain is much better soluble in n-alkanes as the polymer with cyclic side chain.

n–Alkanes with longer chain length act as θ–solvents for PHMA. As the Mark-Houwink exponent turned out to be linearly related to the temperature (Fig. 2), the θ-temperatures were determined from the condition a = 0.5 valid for the θ-state. The unperturbed dimensions, expressed as the K_θ value of the Mark-Houwink equation, were calculated as arithmetic mean from $[\eta]_\theta/M^{0.5}$ values established from at least four fractions of different molecular weights.
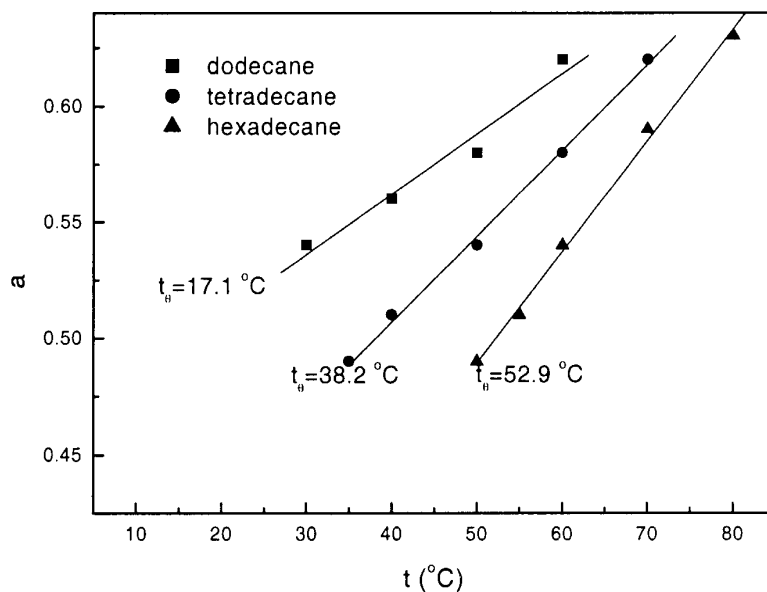
Figure 2 Mark–Houwink exponent a, as a function of temperature for PHMA in n–alkanes

The temperature coefficient of unperturbed dimensions $\dfrac{d\ln\bar{r}_o^2}{dT} = \dfrac{2}{3}\dfrac{d\ln K_\theta}{dT}$ was

obtained graphically ($\dfrac{d\ln\bar{r}_o^2}{dT} = 2.56 \times 10^{-3} \mathrm{deg}^{-1}$) from the temperature dependence of the established K_θ values (Fig. 3). Obtained value is practically identical with the result of the thermoelastic measurements [6].
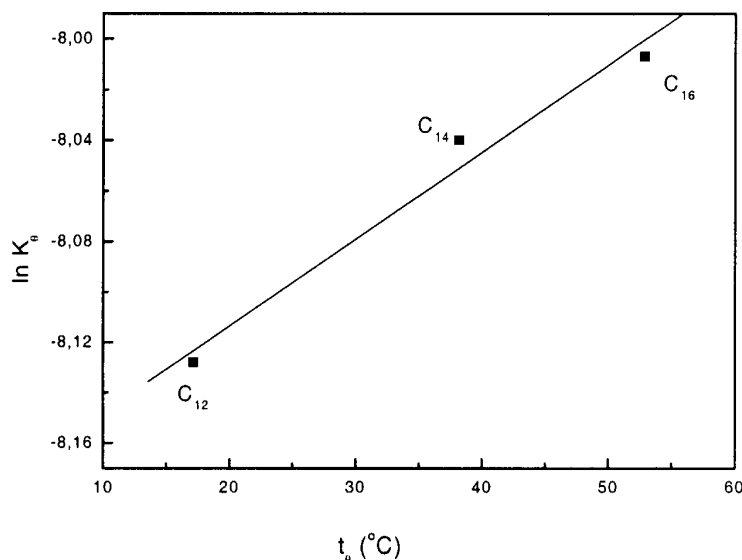
Figure 3 Temperature dependence of the K_θ values for PHMA in n–alkanes, acting as θ–solvents

Recently Bohdanecký and Netopilík [7], when analyzing anomalies in characterizing the theta state of macromolecules with long alkyl side chains, have recommended the Burchard-Stockmayer-Fixman method [8,9]

$$\frac{[\eta]}{M^{0.5}} = K_\theta + c_\eta \ B\, \phi M^{0.5} \qquad (2)$$

with

$$K_\theta = \phi\left(\frac{\bar{r}_o^2}{M}\right)_\infty^{\frac{3}{2}}$$

where c_η is numerical constant, ϕ is the Flory viscosity constant found experimentally [10] to have the value of 2.5 ($\pm$ 0.1)$\times 10^{21}$, B is a characteristic of the polymer-solvent interaction and $\bar{r}_o^2$ is the unperturbed mean square end-to-end distance

for the elimination of the excluded volume effects by extrapolating the intrinsic viscosity data to $M^{0.5}=0$ and stressed that the existence of a minimum in this plot at low values of M indicates the influence of chain thickness on K_θ values determination. Typical plots of Eq. (2) reproduces Fig. 4 and the obtained K_θ are summarized in Table 3.
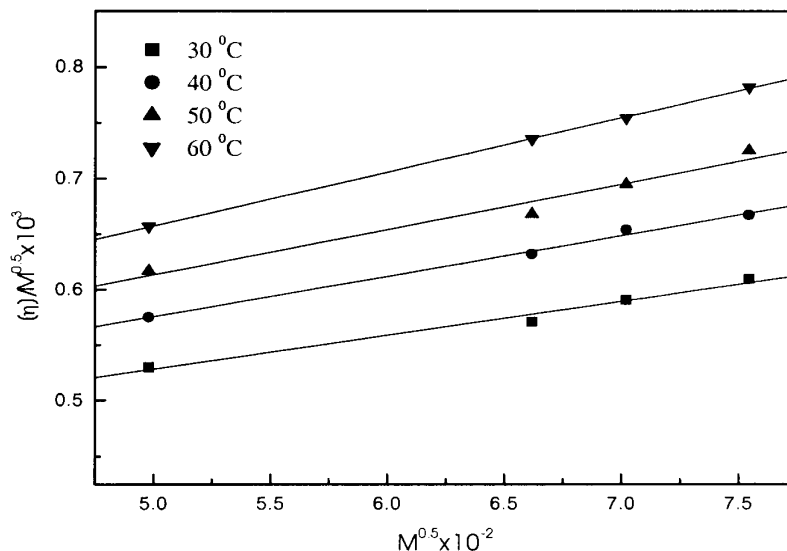
Figure 4 Burchard–Stockmayer–Fixman plots for poly(n–hexyl methacrylate) in n–octane at different temperatures

Table 3 Values of K_θ for PHMA as a function of temperature

t [°C]	$K_\theta \times 10^4$			
	heptane	octane	decane	dodecane
30	3.91	3.76	3.56	3.57
40	4.08	3.94	3.82	3.94
50	4.20	4.08	3.89	4.06
60	4.25	4.14	4.22	4.14

The linear character of the dependencies in Fig. 4 is indicative of an excluded volume effect and confirms that the influence of chain thickness is absent.

A potential contributing factor to the alteration of polymer flexibility is the interaction of the longer side chains and such interactions could lead to orientationally ordered structures. This will influence the polymer molecular parameters such as characteristic ratio, C_∞, calculated from the K_θ values (Table 3).

$$C_\infty = \left(\frac{\overline{r}_o^2}{M} \right)_\infty \left(\frac{m_o}{2l_b^2} \right) \qquad (3)$$

where m_o is the molecular weight of the monomeric unit, l_b is the main chain C–C bond ($l_b = 1.5 \times 10^{-8}$ cm) [11].

The obtained value $C_\infty = 10.2 \pm 0.2$ is in good agreement with other presented results ($C_\infty = 10.1–10.5$) [12]. The characteristic ratio of vinyl polymers assumes value from

$C_\infty=6.6$ (poly(methyl methacrylate)) [13] up to $C_\infty=23.6$ (poly(n−docosyl methacrylate)) [12], what characterizes PHMA as typical flexible chain with very weak interaction between side chains.

References

1. Polymer Handbook, 4th Ed. (1999) John Wiley&Sons, New York
2. Wagner HL (1987) J Phys Chem Ref Data 16:165
3. Chinai SN (1957) J Polymer Sci 25:413
4. Lath D, Bohdanecký M (1977) J Polymer Sci, Polymer Lett Ed 15:555
5. Lath D, Sedlák K, Lathová E, Florián Š (1986) Polymer Bull 16:453
6. Tobolsky AV, Carlson DW, Indictor N (1961) J Polymer Sci 54:175
7. Bohdanecký M, Netopilík M (1995) Polymer 36:3377
8. Burchard W (1961) Makromol Chem 50:20
9. Stockmayer WH, Fixman M (1963) J Polymer Sci C 1:137
10. Miyake Y, Einaga Y, Fujita H, Fukada M (1980) Macromolecules 13:558
11. Flory PJ (1969) Statistical Mechanics of Chain Molecules, Interscience Publ., New York
12. Xu ZD, Hadjichristidis N, Fetters L (1984) Macromolecules 17:2303
13. Schulz GV, Kirste R (1961) Z Phys Chem (Frankfurt) 30:171