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The behaviour of poly(2-ethylhexyl acrylate) in dilute solution: viscosity measurements

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SUMMARY

Linear macromolecules of the poly(2-ethylhexyl acrylate) were prepared by solution polymerization in toluene at 12 °C, using azobisisobutyronitrile as initiator. The polymer was fractionated and the fractions characterized by the methods of light scattering, osmometry and viscometry. Mark-Houwink-Sakurada relations at 25°C in solvents of different thermodynamical quality have been determined.

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 polyacrylic esters, though many of them have found various practical applications.

Poly(2-ethylhexyl acrylate), an important part of pressure sensitive adhesives and high-impact additives mainly in the form of the copolymers, has been characterized in solution only recently (3,4) and the study is limited to tetrahydrofuran solutions and to the determination of Mark-Houwink-Sakurada relation constants, using size exclusion chromatography measurements on polydisperse samples. The reliability of the constants obtained depend on the precision of the universal calibration and on the efficiency of the separation system.

The aim of our contribution is to prepare linear 2-ethylhexyl acrylate macromolecules and to characterize them in solvents differing in the thermodynamical quality, using methods of fractionation, light scattering, osmometry, viscometry and differential refractometry.

EXPERIMENTAL

Preparation of the polymer

Linear macromolecules can be prepared in such system, where substitution reactions of all free radicals with the polymer formed are negligible. This can be achieved by lowering the temperature of the polymerization, using the initiator, whose primary radicals do not react by the substitution and by performing the polymerization in the system with low polymer concentration. Using these principles, poly(2-ethylhexyl acrylate) of $M_w=2.26\times10^6$ was prepared by solution polymerization in toluene at 12 °C, using azobisisobutyronitrile as initiator. Monomer conversion was approximately 10 %.The polymer was isolated from the solution by precipitation with excess of the methanol, cooled by dry carbon dioxide and dried in vacuo.

The fractions of the polymer were obtained by successive addition of methanol to toluene solution. Using this procedure 25 fractions were obtained and used for determining Mark-Houwink-Sakurada relations in selected solvents.

Applied methods

Light scattering measurements were carried out in a light scattering instrument Brice-Phoenix, Model 2000 using monochromatic light with the wave length of 436 nm. Fresh distilled n-heptane was used as a solvent. The light scattering data were evaluated by the usual double extrapolation plot due to Zimm.

The refractive index increments were determined by a Brice-Phoenix differential refractometer for different solvents and are summarized in Table 1. The application of the Gladstone-Dale rule to the data of Table 1 gave the polymer refractive index 1.476.

TABLE 1 Refractive index increments of poly(2-ethylhexyl acrylate) at wave length 436 nm

Solvent	Refractive index	Refractive index increments, cm^3g^{-1}
Butanone	1.3850	0.101
n-Heptane	1.3878	0.096
Tetrahydrofuran	1.4134	0.070
Toluene	1.5151	-0.040
Chlorobenzene	1.5422	-0.072

Osmotic measurements were performed with Hewlett-Packard automatic membrane osmometer in toluene. From the light scattering and osmotic measurements of selected fractions their polydispersity expressed as the ratio of weight to number average molecular weight was determined. The average values of the $M_w/M_n=1.2$ were obtained.

Viscometric measurements were done on an Ubbelohde viscometer with a curved capillary (5) at 25 °C. For each fraction solutions of several different concentration were prepared and the viscosity was measured.

Extrapolation to infinite dilution was carried out in order to obtain the limiting viscosity numbers $[\eta]$. For the highest molecular weights appropriate shear corrections were applied, as the lowering of the $[\eta]$ values up to 15 % was found by using the multi-bulb Ubbelohde viscometer. All the experimental data are summarized in Table 2.

TABLE 2 Experimental data of the light scattering and viscosity measurements at 25 °C

Solvent	$[\eta]$, cm^3g^{-1}	$M_w x10^{-6}$
Cyclohexane	339	5.16
	245	3.18
	190	2.31
	123	1.22
	85	0.678
Tetrahydrofuran	213	2.11
	161	1.44
	144	1.10
	98	0.661
	66	0.370
Toluene	368	4.15
	229	2.66
	166	1.53
	114	0.695
	77	0.446
n-Heptane	238	4.81
	223	3.60
	173	2.70
	132	1.96
	112	1.28
n-Decane	234	5.16
	193	3.18
	130	1.96
	104	1.30
	61	0.53
Butanone	160	4.81
	109	2.31
	80	1.25
	59	0.661
	45	0.446

RESULTS

Solubility of the polymer

According to the solubility tests poly(2-ethylhexyl acrylate) is soluble in a variety of solvents. The polymer was found to be soluble in alkanes, aromatic hydrocarbons, halogenated aliphatic and aromatic hydrocarbons, ketones and esters. Thermodynamical quality of the solvents selected was characterized by viscometry measurements on unfractionated sample and the result is summarized in Table 3.

TABLE 3 Limiting viscosity numbers of the unfractionated poly(2-ethylhexyl acrylate) sample of $M_w=2.26\times10^6$ and $M_w/M_n=2.4$ in different solvents at 25 °C

Solvent	$[\eta]$, cm^3g^{-1}
Tetrahydrofuran	223
Toluene	220
Chlorobenzene	214
Cyclohexane	208
Bromobenzene	190
Tetralin	172
n-Heptane	163
n-Decane	157
Butanone	96

Mark-Houwink-Sakurada relation

The dependence of the limiting viscosity number on the molecular weight is given by the equation

$$[\eta] = K\ M^a$$

with K, which is a constant for a certain polymer in a given solvent at a given temperature. The exponent a has values between 0.5 and 1.0.

Figure 1 and Table 4 show $[\eta]$ - M_w relations for poly(2-ethylhexyl acrylate) in the solvents, differing in their thermodynamical quality to the polymer at 25 °C.

The comparison of the Penzel and Goetz $[\eta]$ - M_w relation in tetrahydrofuran: $[\eta] = 11.1\times10^{-3}\ M_w^{0.68}$ with that determined in this work (Table 4) shows a good agreement, giving a valid Mark-Houwink-Sakurada equation for a broad region of the molecular weights. The results obtained from GPC measurements in n-heptane and tetrahydrofuran were generally higher than from direct ones, suggesting probably that the amount of the analyzed polymer homologs was not high enough.

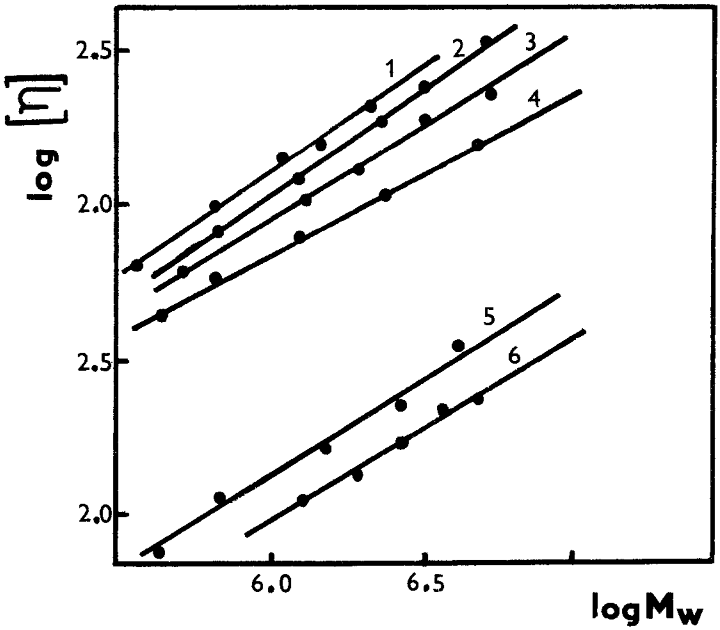

Fig. 1 Mark-Houwink-Sakurada relations for poly(2-ethylhexyl acrylate) in different solvents at 25 °C
1 - tetrahydrofuran, 2 - cyclohexane,
3 - n-decane, 4 - butanone, 5 - toluene,
6 - n-heptane

TABLE 4 The constants of the Mark-Houwink-Sakurada relations for poly(2-ethylhexyl acrylate) in different solvents at 25 °C

Solvent	$K \times 10^3$	a	Regression coefficient
Cyclohexane	8.3	0.69	0.9995
Tetrahydrofuran	12.4	0.67	0.9985
Toluen	16.4	0.65	0.9906
n-Heptane	17.4	0.62	0.9848
n-Decane	20.5	0.61	0.9968
Butanone	52.1	0.52	0.9989

In the forthcoming publication unperturbed dimensions of the poly(2-ethylhexyl acrylate) and their temperature coefficient will be discussed.

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