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Solution Properties of Poly(2-methoxyethyl methacrylate)

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ABSTRACT: Solution properties of poly(2-methoxyethyl methacrylate) (PMEMA) were investigated by light scattering, viscometry, and gel-permeation chromatography (GPC). The refractive and density increments and the apparent partial specific volumes of PMEMA in various solvents were determined. The properties of cosolvent mixtures for PMEMA are discussed. The constants of the Mark—Houwink equation for PMEMA fractions were determined in methyl ethyl ketone and tetrahydrofuran. The steric factor of PMEMA was determined from viscometric data. Comparison of the molecular parameters of PMEMA calculated from the GPC data and measured by an independent method confirmed the validity of the universal calibration. The solution properties of PMEMA and poly(methyl methacrylate) are compared.

KEY WORDS Cosolvency / Density and Refractive / Index Increments / Poly(2-methoxyethyl methacrylate) / Steric Factor / Relationships of Viscosity and Molecular Weight / Light Scattering / Second Virial Coefficient / 1,1,1-Trifluoro-2-chloro-2-bromoethane / Gel-Permeation Chromatography / Viscometry /

Poly(2-methoxyethyl methacrylate) (PMEMA) is one of the polymers which both as a homopolymer or a constituent of copolymers have been used for many industrial[1] or medical purposes.[2–4] The properties of PMEMA have been investigated in a number of recent papers. Attention have been concentrated mainly on the anionic polymerization of 2-methoxyethyl methacrylate,[5–7] for which an interesting dependence of the microstructure of the polymer on conversion was found. Radical polymerization has also been studied.[8,9] Unlike many papers dealing with the mechanical properties of PMEMA,[10–13] information on the solution properties of this polymer is fragmentary.[14] This prompted us to investigate the solution properties in more detail.

EXPERIMENTAL

Polymer Synthesis, Solvents

The monomer was prepared by esterification of methacrylic acid (Fluka AG, Switzerland) with ethylene glycol monomethyl ether (Lachema, Czechoslovakia). Both chemicals were of "pure" quality grade (99.50 and 99.97% resp.); ethylene glycol monomethyl ether was distilled before use in the presence of cuprous chloride in order to remove peroxidic compounds. Esterification was catalyzed with a small amount of *p*-toluenesulphonic acid. The forming monomer was stabilized with hydroquinone. Water formed during the reaction was removed by azeotropic distillation with benzene. Residues of unreacted starting compounds and the stabilizer were extracted with aqueous sodium hydroxide. The raw product stabilized with 0.1% of octylpyrocatechol was distilled at reduced pressure on a laboratory column, bp 67—68°C/1.6*kPa* (12 mmHg), yield 40%. The purity of the product (99.95%) was verified by gas chromatography, as was that of the starting compounds.

The polymerization was carried out in toluene (50 vol%) at 60°C under nitrogen up to a 40-% conversion. The initiator, azo-bisisobutyronitrile, was twice recrystallized from methanol.

The PMEMA fractions were obtained by fractionation of several samples having different molecular weights with the system toluene—ethanol at 27°C. The high-molecular-weight fractions were reprecipitated from the system acetone—methanol; the low-molecular-weight fractions, which were partly soluble in methanol, were reprecipitated from the system acetone—water. Nonpolar precipitants (*n*-heptane, cyclohexane, etc.) were not suitable for fractionation, because the polymer gel strongly adhered to the glass parts of the fractionation vessel and was difficult to isolate. Polar solvents (especially lower alcohols) were not very effective, but they were found to be useful in the separation of high-molecular-weight samples. No fully satisfactory precipitant was found for samples with lower molecular weights, and the use of water in the reprecipitation of such samples was only a kind of compromise.

Most of the solution properties of PMEMA were determined with methyl ethyl ketone (MEK) (Reanal, Hungary) and tetrahydrofuran (THF) (VEB Laborchemie Apolda, German Democratic Republic) as solvents. Both solvents were reagent grade and distilled on laboratory columns; to THF, cuprous chloride and potassium hydroxide were added to remove peroxidic compounds and water. The other solvents used for characterization, *i.e.*, toluene, nitrobenzene, and tetrachloromethane were also reagent grade (Lachema, Czechoslovakia); 1,1,1-trifluoro-2-chloro-2-bromoethane (halothane) was a pharmaceutical product (Spofa, Czechoslovakia) stabilized with 0.1% of thymol.

Experimental Methods

The refractive index increments were measured with a Brice-Phoenix BP-2000-V model differential refractometer at 25.0±0.01°C and wavelength 546 nm. The apparatus was calibrated with aqueous potassium chloride solutions.

The density increments were calculated from the densities of polymer solutions and solvents measured with a digital densitometer, DM-02-C, manufactured by A. Paar K. G. (Graz, Austria). The apparatus was calibrated with a number of liquids of known density. The concentration of polymer solutions for refractometric and densitometric measurements did not exceed 1 wt%.

The polymer samples were characterized by light scattering with a commercial SOFICA type 42.000 apparatus for angles from 30° to 150° with unpolarized primary light, wavelength 546 nm, at 25.0±0.1°C. The Rayleigh ratio for benzene was taken to be $16.3 \times 10^{-6}\ \mathrm{cm}^{-1}$.

The solutions were optically purified by centrifugation in a preparative Spinco model L ultracentrifuge, in a swinging bucket rotor SW 25.1 at 15,000 rpm for 60 min directly in the light scattering cells.[15] Solutions of polymers with molecular weight lower than 3×10^5 were purified by pressure filtration through bacterial sintered glass filters, Jena G5.

Intrinsic viscosities were measured with a modified Ubbelohde viscometer at 25.0 and 40.0±0.01°C.

GPC measurements were carried out with an apparatus built at this Institute, using a Waters type R 403 differential refractometer. Six separation columns packed with porous silica gel Sphérosil E, D, and B (Produits Chimiques, France) were thermostated to 25.0±0.1°C. The flow-rate of THF, the concentration of the injected PMEMA sample, and the total injected solution volume were chosen so as to suppress undesirable phenomena, particularly the concentration effect. The separation system was calibrated with polystyrene standards (Waters Ass., USA). The molecular parameters of the PMEMA were calculated from a universal calibration curve[16] without correction for the dispersion of the chromatographic wave.

RESULTS AND DISCUSSION

Behavior in Single Solvents

The solubility parameter of PMEMA calculated according to Small[17] is $18.8\ (\mathrm{J/m}l)^{1/2}$ $(9.2\ (\mathrm{cal/m}l)^{1/2})$. This value is virtually identical with the solubility parameters reported for poly(methyl methacrylate) (PMMA);[17] the solubility behavior of PMMA and PMEMA in organic solvents is also very similar. PMEMA is quite soluble in aromatic and halogenated hydrocarbons, with the exception of tetrachloromethane, in lower esters, ketones, nitriles, and in formic and glacial acetic acid. Aliphatic ethers and saturated hydrocarbons are an example of typical nonsolvents. Alcohols also act as nonsolvents

Table I. Refractive index increments dn/dc in ml/g (546 nm), density increments dρ/dc, and apparent partial specific volumes $\bar{v}_p$ in ml/g for PMEMA in various solvents at 25°C

Solvent	dn/dc	dρ/dc	$\bar{v}_p$[a]
Methyl ethyl ketone	0.108	0.332	0.836
Tetrahydrofuran	0.078	0.260	0.836
Toluene	0.000	0.276	0.840
Nitrobenzene	−0.058	−0.013	0.845
Halothane	0.125	−0.476	0.795

[a] Calculated from density increments according to ref 31.

for PMEMA at room temperature, but already at a slightly elevated temperature PMEMA, unlike PMMA, is completely soluble in both methanol and ethanol; the dissolving power of alcohols decreases with increasing length of their hydrocarbon chain. PMEMA is insoluble in water.

In more detail those solvents were investigated which could be important in the PMEMA characterization and in the study of its solution properties or in which PMEMA exhibited an interesting behavior (Table I).

Methyl ethyl ketone and tetrahydrofuran are thermodynamically good solvents of PMEMA. The sufficiently high refractive index increment of PMEMA in MEK allows a reliable molecular-weight determination by light scattering. THF is commonly used in the characterization of polymers by means of GPC. Both solvents are also suited for the viscometric-molecular-weight determination.

Toluene is an isorefractive solvent of PMEMA: this has been proved both by the zero excess light scattering (the intensities of light scattered from a toluene solution of PMEMA and from pure toluene are identical) and by determination of the zero refractive index increment (Table I). Isorefractive solvents are especially convenient in the investigation of copolymers or homopolymer mixtures by light scattering.[18]

Of the solvents under investigation, nitrobenzene is the closest to an isopycnic solvent. The density increment of PMEMA in nitrobenzene is nevertheless slightly negative (Table I).

Thermodynamically, 1,1,1-trifluoro-2-chloro-2-bromoethane (halothane) is one of the best solvents of PMEMA. The second virial coefficients of PMEMA in this solvent, determined by light scattering, assume for $M_w=10^5$—10^6 values between 7 to 8×10^{-4} mol ml/g^2. The use of halothane as a polymer solvent may be advantageous particularly in those cases where the solvent should possess at the same time high density and low refractive index[19] (for halothane, $d_4^{20}=1.872$ g/ml, $n_D^{20}=1.370$, cf.[20]). Halothane is also readily available because of its wide application as an inhalation anaesthetic in medicine.

The dependence of experimentally obtained refractive index increments of PMEMA on the refractive indexes of solvents is linear (Figure 1) and satisfies the relationship

$$\frac{\mathrm{d}n}{\mathrm{d}c}=\bar{v}_p(n_s-n_p) \qquad (1)$$

where dn/dc, $\bar{v}_p$, n_s, and n_p respectively are the refractive index increment, the apparent partial specific volume of the polymer, and the refractive indexes of the solvent and polymer. Only the refractive index increment of PMEMA in halothane is anomalously high and lies above

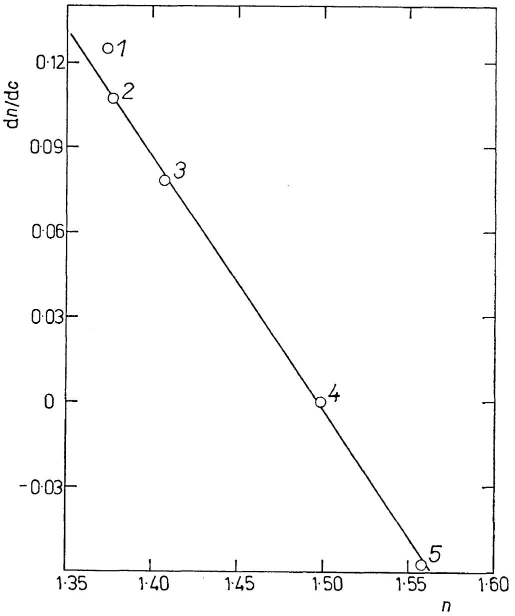

Figure 1. Dependence of the refractive index increments of PMEMA dn/dc in ml/g on the refractive index of solvent, n. Refractive indexes are taken from ref 32: 546 nm; 25°C; 1, halothane; 2, MEK; 3, THF; 4, toluene; 5, nitrobenzene.

the straight line plotted by the least-squares method through the other experimental points, although according to eq 1 it should be situated below this line because of its low partial specific volume (Table I). Hence we infer that there is a change in the polarizability of the polymeric molecule of PMEMA in halothane compared to the other solvents; this might be explained by a specific interaction of the polymer with the solvent (*e.g.*, complex formation and like). Assuming the existence of such interactions, one may also explain the low partial specific volume and rather high second virial coefficients of PMEMA in halothane.

Cosolvent Mixtures for PMEMA

Mixtures of methanol or ethanol with a certain amount of water are able to dissolve PMEMA at room temperature, that is, they are cosolvent systems for PMEMA.

Compositions of the methanol—water θ-mixtures were estimated by extrapolation of the dependences of the cloud points to a 100-% polymer content at 25°C. The polymer was dissolved in a mixture of both solvents (80-vol% methanol); turbidity was achieved by adding methanol or water (Figure 2). Two θ-solvent compositions were obtained with volume fractions of methanol 0.72 and 0.89. Within the composition range restricted by these values, PMEMA is completely soluble at 25°C.

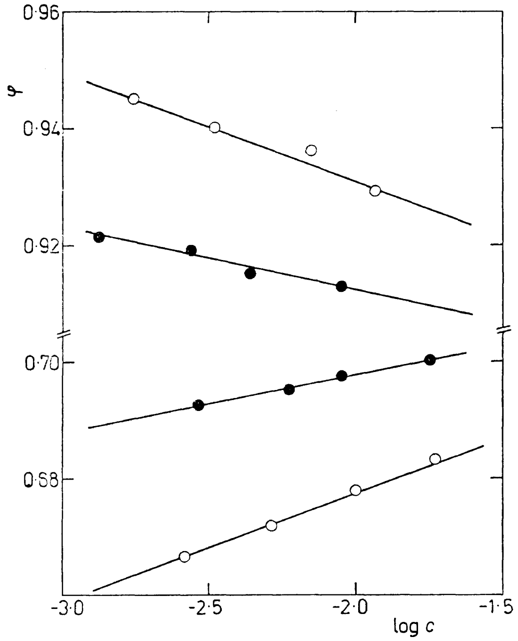

Figure 2. Dependence of the volume fraction of methanol φ in the cloud point on polymer concentration, c, in g/m*l* in the cloud point: 25°C; M_w, 1.71×10^5 (○); 1.40×10^6 (●).

Methanol and water form an "asymmetric" pair of solvents, *i.e.*, the solubility parameters of both components of the cosolvent mixture have values higher than the solubility parameter of the polymer. Cowie, *et al.*,[21] described an analogous "asymmetric" system: polystyrene—acetone—cyclohexanol. A common case of the cosolvent effect of a mixture of two nonsolvents can be demonstrated for PMEMA in mixtures of methanol and tetrachloromethane. Here the solubility parameter of the polymer lies between the values of each component of the cosolvent mixture, and the cosolvency can be anticipated. The analogy between the solubility behavior of PMEMA and PMMA mentioned for single solvents appears also in this connection because the same system methanol—tetrachloromethane is also a cosolvent pair for PMMA.

Besides the cosolvent mixtures mentioned above, PMEMA is also soluble in concentrated aqueous solutions of some inorganic salts, such as zinc bromide and iodide.[22]

Molecular Parameters of PMEMA

The treatment of viscometric data (Table II) yielded the following PMEMA relationships between intrinsic viscosity and molecular weight (Figure 3):

$$[\eta]=7.3_4\times10^{-5}M_w^{0.71} \quad \text{(MEK, 25°C)} \qquad (2)$$

$$[\eta]=7.5_7\times10^{-5}M_w^{0.71} \quad \text{(THF, 25°C)} \qquad (3)$$

For PMMA, under the same conditions, the Mark—Houwink equation constants, $K=6.8\times10^{-5}$ and $a=0.72$ in MEK[23] and $K=9.3\times10^{-5}$ and $a=0.72$ in THF,[24] were obtained. A comparison reveals a pronounced similarity between the solution behavior of both polymers, PMEMA and PMMA, at least for the solvents mentioned.

The dependence of the second virial coefficient of PMEMA fractions on the molecular weight in MEK, determined by light scattering (Table II, Figure 4), can be described as:

$$A_2=3.3\times10^{-2}M_w^{-0.36} \quad \text{(MEK, 25°C)} \qquad (4)$$

Table II. Results of light scattering, GPC, and viscometric measurements of PMEMA solutions at 25°C[a]

$M_w\times10^{-5}$	$M_w\times10^{-5}$	(M_w/M_n)	$A_2\times10^4$	$[\eta]$			$[\eta]$
LS, MEK	GPC, THF	GPC, THF	LS, MEK	MEK	CCl_4[b]	THF	GPC, THF
0.45	0.37	1.48	8.10	0.145		0.159	0.13
0.68	0.65	1.20	6.20	0.203		0.216	0.20
0.96	0.88	1.32	5.07	0.251		0.254	0.24
1.00	0.91	1.19	5.04	0.262		0.275	0.25
1.33	1.27	1.25	4.55	0.319	0.172	0.339	0.32
1.81	1.69	1.27	4.16	0.390		0.426	0.39
2.84	2.80	1.36	2.85	0.561		0.580	0.55
2.93	2.74	1.35	3.74	0.558		0.576	0.54
4.38	4.38	1.60	2.41	0.710	0.298	0.734	0.75
7.67	8.63	1.55	2.60	1.046	0.352	1.141	1.21
10.2	11.9	1.32	2.20	1.368		1.496	1.57
20.6	21.9	1.23	1.76	2.235	0.466	2.363	2.43

[a] M is molecular weight, A_2 the second virial coefficient in mol ml/g^2, $[\eta]$ intrinsic viscosity in dl/g, and LS means light scattering.

[b] 40°C.

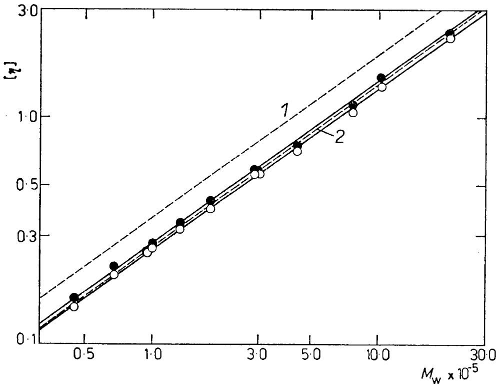

Figure 3. Dependence of intrinsic viscosity $[\eta]$ in dl/g on molecular weight, M_w, for PMEMA (——) in THF (●) and MEK (○) and its comparison with an analogous dependence for PMMA (----) in THF (1) and MEK (2) at 25°C.

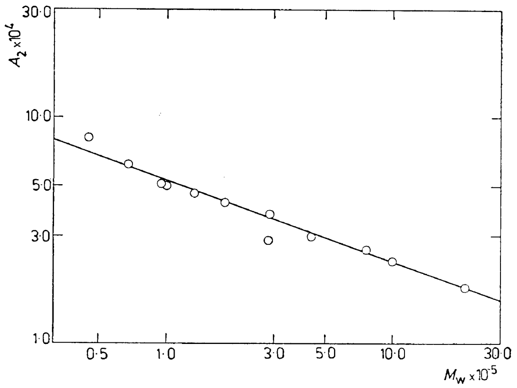

Figure 4. Dependence of the second virial coefficient A_2 in mol ml/g^2 on molecular weight M_w of PMEMA in MEK at 25°C.

The viscometric data were used for the calculation of the steric factor characterizing the short-range interactions in the polymer chain. The needed value of the viscometric constant K_0 corresponding to the constant of the Mark—Houwink equation of a polymer in a θ-solvent was estimated from the intrinsic viscosities of PMEMA in MEK and THF by means of several extrapolation procedures[25–27] recommended for thermodynamically good solvents. All the plots employed yielded the constant $K_0=(5.5\pm0.2)\times10^{-4}$ dl/g, irrespective of the type of solvent (Figure 5), which corresponds to a steric factor $\sigma=2.30\pm0.03$. Because of the polydispersity of the fractions (Table II), the Flory constant was taken as $\Phi_0=2.68\times10^{21}$. The constant K_0 obtained by plotting data for PMEMA in tetrachloromethane at 40°C (Figure 5) does not differ within experimental error from the K_0 values obtained for the other solvents at 25°C.

Since the methoxy group of PMEMA is more polar than the alkyl groups but less polar than the hydroxy group, the steric factor of PMEMA

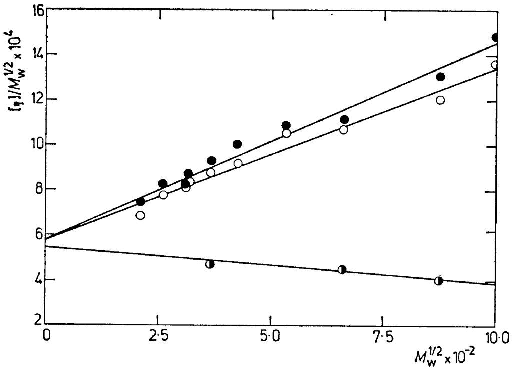

Figure 5. Determination of viscometric constant K_0. Plot $[\eta]/M^{0.5}=1.05K_0+KM^{0.5}$ for $1.2<\alpha_\eta<2.3$ according to ref 26 for THF (●) and MEK (○) at 25°C, and $[\eta]/M^{0.5}=K_0+K'M^{0.5}$ for $\alpha_\eta<1.6$ according to ref 33 for tetrachloromethane (◑) at 40°C; α_η, the viscosity expansion coefficient; K, K', constants.

is higher than that of *n*-alkyl methacrylates with similarly long side chains (*e.g.*, for *n*-butyl methacrylate,[28] $\sigma=1.96$), and lower than the steric factor of poly(2-hydroxyethyl methacrylate)[29] ($\sigma=2.55$).

The determination of some molecular parameters of PMEMA fractions by GPC was made to confirm the assumption of the validity of the so-called universal calibration for PMEMA. The applicability of the universal parameter was experimentally verified for PMMA,[16] while for PMEMA samples the validity of the universal calibration was indicated only in a restricted interval of molecular weights.[14]

The molecular parameters of PMEMA samples were calculated by means of the universal calibration curve constructed for polystyrene standards with a narrow molecular-weight distribution, for which the Mark—Houwink equation holds in the form[30]

$$[\eta]=1.17\times10^{-4}M^{0.717} \quad \text{(THF, 25°C)} \qquad (5)$$

and the experimentally determined constants of the Mark—Houwink eq 3 for PMEMA in THF at 25°C.

The agreement between the M_w and $[\eta]$ values calculated from the GPC data and measured directly by light scattering and viscometrically in THF (Table II) confirms the validity of the universal calibration. The molecular weights of PMEMA fractions calculated from the GPC data are somewhat lower than those determined directly by light scattering, especially for lower molecular weights, but most cases these differences are comparable with the experimental error.

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