Light scattering characterization of organotin polymers: 1. Tributyltin acrylate copolymer Cutinox-1000*

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Laser light scattering including both elastic (integral) and quasielastic measurements, supplemented by intrinsic viscosity data, has been used to characterize a tributyltin acrylate copolymer commercially known as Cutinox-1000 in dilute solution. Four solvents differing in their thermodynamical quality and optical properties were used. Chemical composition heterogeneity of the investigated sample was estimated to be sufficiently small not to influence significantly results of light scattering measurements. Coupled integral and quasielastic light scattering methods were used to determine the molecular weight distribution function, from which the polydispersity of the investigated copolymer sample was estimated to be $\bar{M}_w/\bar{M}_n = 2.1$. Determined molecular properties were in reasonable agreement with some theoretical predictions. Conformational parameters, such as the steric factor σ, statistical segment length and $\bar{R}_H/\bar{R}_G$ ratio, as compared with poly(methyl methacrylate) values suggest some small increase of the copolymer rigidity, probably due to steric hindrance caused by the large metalloorganic side groups.

(Keywords: light scattering; characterization; organotin polymers)

INTRODUCTION

Organotin polymers form an important class of materials with many applications, e.g. in making antifouling and self-polishing coatings for underwater structures. These polymers have very interesting properties especially as binders in such coatings[1].

However, very little is known about the polymerization and copolymerization behaviour of respective monomers and about physico-chemical properties of organotin polymers in solution.

A representative of this class of polymers is a tributyltin acrylate copolymer commercially available from ACIMA (Buchs SG), Austria under the registered trade-mark Cutinox-1000. An experimental study of hydrodynamic and rheological properties of this copolymer seems to be interesting both for applied and scientific standpoints, particularly because of the possible influence of the big side groups on the copolymeric chain conformation.

EXPERIMENTAL

Cutinox-1000 is a two-component copolymer consisting of methyl methacrylate (component A) and tributyltin acrylate (component B) monomers[2]. It is commercially available as a 50% solution in aromatic white spirit. The pure copolymer, for simplicity termed Cutinox, was precipitated from the solution into a methanol–water mixture or alternatively it was recovered by solvent evaporation. It was then dissolved in benzene or xylene and reprecipitated with petroleum ether at 313–323 K, repeating this procedure several times. Prepared in such a way, the copolymer appears as an amorphous solid. The glass transition temperature T_g of vacuum-dried Cutinox films cast from various solvents was determined using a DuPont 1090 differential scanning calorimeter at a heating rate of 20 K min^{-1}. The representative differential scanning calorimetry (d.s.c.) trace is shown in *Figure 1*, from which a value of $T_g = 261$ K was obtained.

On the basis of both spectroscopic data (which will be published in detail elsewhere), and information obtained from the producer[2], the chemical composition of the prepared Cutinox samples could be determined. The weight fraction of component A (methyl methacrylate) was estimated to be $w_A \approx 0.60$–0.73 and for component B (tributyltin acrylate) $w_B \approx 0.27$–0.40.

Four solvents were used in the light scattering experiments reported here: xylene, carbon tetrachloride, acetone and an isorefractive mixed solvent (xylene:propylbenzene, 85:15 v/v). All solvents were pure analytical grade, distilled and purified by standard methods. Five concentrations were prepared by the dilution of one stock solution for each copolymer–solvent system. All final concentrations were within the range from 0.2 to 1.0 g dm^{-3}. Measurements for the mixed solvent system were performed at osmotic equilibrium,

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* Cutinox-1000 is a registered trade-mark for a commercial product of ACIMA Company (Buchs SG), Austria

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that is after 7 days of dialysis at 298 K in a Kratochvíl-type[3] osmometer. For this particular system however, only very small changes in $\partial\tilde{n}/\partial c$ were detected after dialysis (cf. *Table 1*). Solutions were filtered through a 2.2 μm silver metallic membrane filter (Selas Flotronics, USA) immediately before light scattering experiments.

Viscometric measurements were performed in xylene and acetone for more dilute solutions, ranging from 0.02 to 0.25 g dm^{-3}.

Methods of measurement

Solvent refractive indices $\tilde{n}_0$ (*Table 1*) were taken from the literature[4,5] with the exception of the isorefractive solvent, for which the value $\tilde{n}_0 = 1.489$ was obtained experimentally. Specific refractive index increments $\bar{v} = \partial\tilde{n}/\partial c|_{c=0}$ were determined by a Waters 401 differential refractometer modified for static measurements and using a He–Ne laser as a light source of the wavelength, $\lambda_0 = 632.8$ nm. The absorbance of the solutions was established using a C. Zeiss Jena (DDR) Specord u.v.–vis. spectrometer.

Intrinsic viscosities ($[\eta]$) and Huggins coefficients (k') for Cutinox solutions in xylene and acetone (*Table 2*) were measured by standard methods with an Ubbelohde viscometer. All experimental results shown in *Tables 1*, *2* and *3* were obtained at 294 K for carbon tetrachloride solutions (i.e. under theta conditions for this system as evidenced by $A_2 = 0$ obtained from light scattering) and at 298 K for other solvents.

Simultaneous static (integral) and quasielastic (QLS) light scattering measurements were carried out using self-obtained equipment with a He–Ne 35 mW laser as a light source ($\lambda_0 = 632.8$ nm). Both the apparatus and procedures for data evaluation have been described previously[6]. The clipped homodyne autocörrelation function (ACF)[7,8] is computed by means of the 64-channel digital correlator:

$$C(q,c,t) = \frac{\langle n(t) n_k(0) \rangle}{\langle n \rangle \langle n_k \rangle} \tag{1}$$

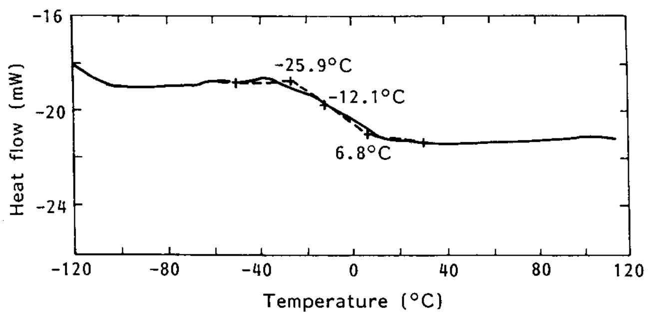

Figure 1 D.s.c. diagram for Cutinox film

Table 2 Results of integral light scattering measurements for Cutinox dilute solutions

Solvent	$\bar{M}_w^{app} \times \bar{v}^2$ (cm^6 g^{-1} mol^{-1})	$\bar{M}_w \times 10^{-5}$ (g mol^{-1})	$\bar{A}_2 \times 10^4$ (cm^3 mol g^{-2})	$\bar{R}_{Gz}$ (nm)
Acetone (298 K)	–	3.17	1.95	47.4
Carbon tetrachloride (294 K)	–	3.20	0.00	39.8
Xylene (298 K)	2.76	3.10	0.1	40.5
Isorefractive solv. (298 K)	12.36	–	0.0	–

Table 3 Results of quasielastic light scattering measurements for Cutinox dilute solutions

Solvent	$\bar{D}_{oz} \times 10^7$ (cm^2 s^{-1})	$\bar{R}_H$ (nm)	$\bar{R}_H/\bar{R}_G$	$\bar{M}_w/\bar{M}_n$
Acetone (298 K)	2.01	35.0	0.738	–
Carbon tetrachloride (294K)	0.859	28.6	0.719	2.1
Xylene (298 K)	1.175	30.7	0.758	–

where t is the delay time, and $n(t)$ and $n_k(t)$ are the total and clipped number of photodetections per sampling time $(t, t+\Delta t)$, respectively (i.e. $n_k = 0$ for $n = 0$ and $n_k = 1$ for $n > 0$). As is evident from equation (1), the measured ACF is a function of the concentration c and of the scattering vector value q, associated with θ, the actual scattering angle: $q = (4\pi\tilde{n}_0/\lambda_0)\sin(\theta/2)$. The baseline level B

$$B = \lim_{t\to\infty} C(q,c,t) \tag{2}$$

and the average number of photodetections per sampling period $\langle n(q,c) \rangle$ are also determined. The latter quantity is proportional to the normalized integral intensity of the scattered light, usually determined during classical static light scattering experiments.

Measured values of $\langle n(q,c) \rangle$ were treated by the conventional Zimm double extrapolation method[6,9] to obtain static properties of solute macromolecules; which are shown in *Table 2*, i.e. their weight average molecular weight $\bar{M}_w$, z-average radius of gyration $\bar{R}_{Gz}$ and the second virial coefficient $\bar{A}_2$. An example of a Zimm plot obtained for the Cutinox–carbon tetrachloride system is shown in *Figure 2*.

Measured ACFs were extrapolated[4,6,11] to infinite dilution and zero scattering angle to obtain $y(X)$ values:

$$y(X) = \lim_{\substack{c\to 0 \\ q\to 0 \\ X = q^2 t = \text{constant}}} (C(q,c,t) - B)^{1/2} \tag{3}$$

Table 1 Optical and viscoelastic properties of Cutinox solutions

	Solvent properties		Solution properties					
Solvent	$\tilde{n}_0$	η_0 (mPa s)	$\bar{v}$ (cm^3 g^{-1})	$[\eta]$ (dl g^{-1})	k'	ν_A (cm^3 g^{-1})[b]	ν_B (cm^3 g^{-1})[c]	$\Delta\nu$ (cm^3 g^{-1})[c]
Acetone (298 K)	1.3564	0.316	0.130	0.101	0.360	0.127	0.134–0.138	0.007–0.011
Carbon tetrachloride (294 K)	1.4587	0.950	0.032	–	–	0.023	0.045–0.056	0.022–0.033
Xylene (298 K)	1.4930	0.605	0.002	0.101	0.745	–	–	–
Isorefractive solv. (298 K)[a]	1.4890	–	0.000	–	–	–	–	–

[a] Xylene–propylobenzene mixture (85:15 v/v). $\bar{v} = 0.000$ at osmotic equilibrium (after 7 day dialysis), $\bar{v} = -0.002$ before dialysis
[b] Refractive index increment measured for PMMA solutions
[c] Values estimated from equation (5)

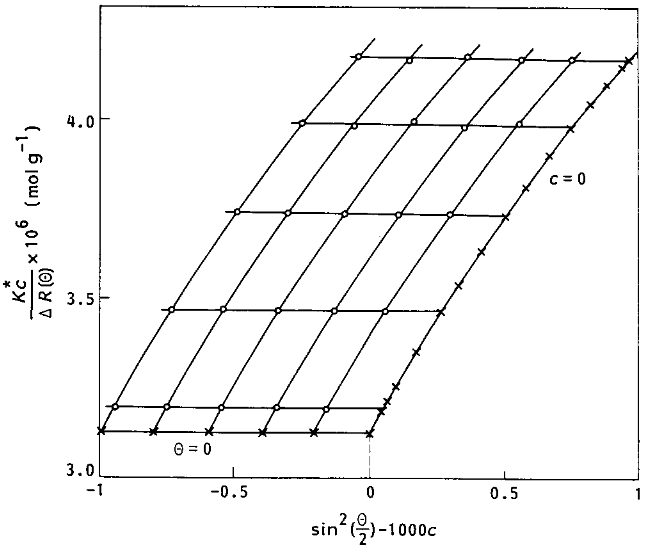

Figure 2 Zimm plot for Cutinox solutions in carbon tetrachloride at 294 K. Only 5 from 15 determined θ=constant lines are shown for the sake of clarity. ○, Experimental points; ×, extrapolated values

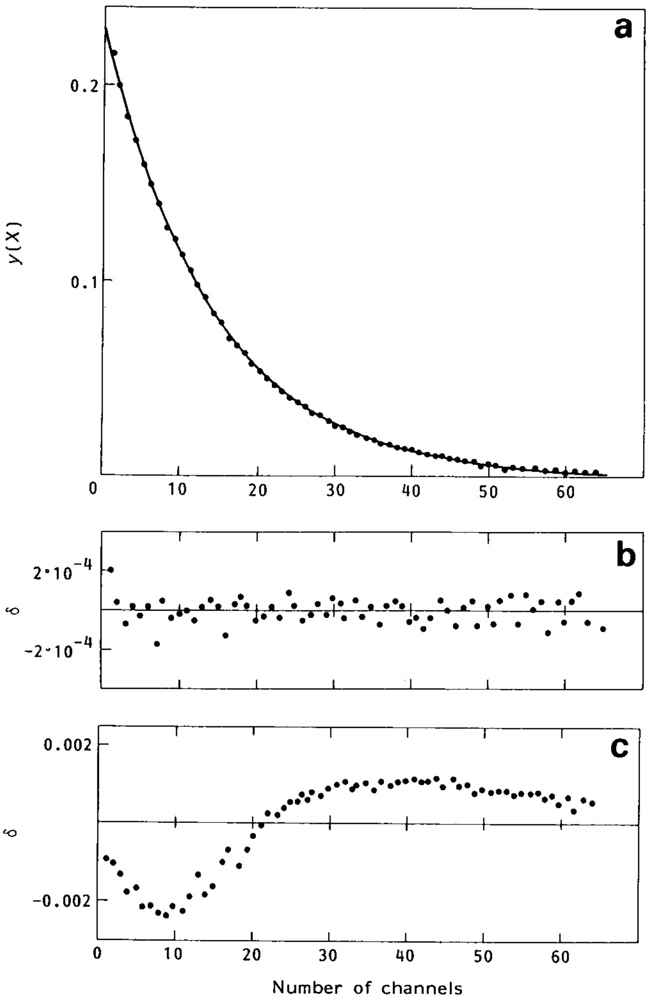

Figure 3 (a) Extrapolated autocorrelation function $y(X)$ obtained from quasi-elastic light scattering experiments for the Cutinox–carbon tetrachloride system. The data points are the experimental values of $y(X)$, and the line is the best fit $\bar{y}(X)$ values calculated from (10) with the $w(M)$ function shown in *Figure 6*. Errors of the best fits $\delta = y(X) - \bar{y}(X)$ are shown for two cases; (b) $\bar{y}(X)$ calculated from equation (10), and (c) $\bar{y}(X)$ is assumed to be a single exponential function

in order to eliminate effects of concentration and intramolecular mobility[7,10]. An example of such an extrapolated $y(X)$ function is shown in *Figure 3a*.

The standard cumulant technique[6,12] was then applied to $y(X)$ functions to obtain extrapolated to infinite dilution z averages of translational diffusion coefficients $\bar{D}_{oz}$. Average values of hydrodynamic radii of solute macromolecules were then computed from the Stokes–Einstein formula;

$$\bar{R}_H \equiv \langle R_H^{-1}\rangle_z^{-1} = \frac{kT}{6\pi\eta_0\bar{D}_{oz}} \qquad (4)$$

where k is the Boltzmann constant, T is temperature and η_0 is solvent viscosity.

RESULTS AND DISCUSSION

Average molecular properties and influences of the chemical heterogeneity

It is well known from light scattering experiments for copolymer solutions that only apparent values of macromolecular properties can generally be obtained[13]. For example, real $\bar{M}_w$ and apparent $\bar{M}_w^{app}$ values of the weight average molecular weight are related to each other as follows:

$$\lim_{\substack{q\to0\\c\to0}} \frac{\Delta R}{K_1 c} = \bar{M}_w^{app}\cdot\bar{\nu}^2 = \bar{M}_w\bar{\nu}^2 + 2P\bar{\nu}\Delta\nu + Q(\Delta\nu)^2 \qquad (5)$$

where ΔR is an experimentally determined excess Rayleigh ratio, $K_1 = (4\pi\tilde{n}_0/\lambda_0)^2$, N_A^{-1} is the optical constant and N_A is the Avogadro number. Note that K_1 defined here does not contain the refractive index increment $\bar{\nu}$. An investigated copolymer sample is assumed to consist of two-component copolymeric species A and B, w_A and w_B being their weight fractions in the sample and ν_A, ν_B the respective specific refractive index increments. Quantities $\bar{\nu}$ and $\Delta\nu$ in equation (5) are then defined as follows:

$$\bar{\nu} = \nu_A w_A + \nu_B w_B, \qquad \Delta\nu = \nu_A - \nu_B \qquad (6)$$

Parameters P and Q establish the measure of the chemical composition heterogeneity of the copolymer: for the sample which is homogeneous according to its chemical composition $Q=0$ and for the opposite case, i.e. for the mixture of two homopolymers with equal molecular weights ($\bar{M}_{wA} = \bar{M}_{wB}$) the maximal possible value $Q = w_A w_B \bar{M}_w$ is reached. The standard method[13] for calculating the real molecular weight $\bar{M}_w$ is based on the fitting of the second order polynomial to the experimentally determined dependence of $\bar{M}_w^{app}$ on $\Delta\nu/\bar{\nu}$. Conditions for the most accurate evaluation of P and Q by means of this 'parabola fitting' method are discussed in reference 14. However, for small compositional heterogeneities this method cannot provide reliable information on P and Q values[15].

Another procedure, i.e. determination of Q value from the single measurement in the isorefractive solvent was originally proposed by Kratochvíl *et al.*[14,16] and developed by Tanaka and coworkers[15,17]. For $\bar{\nu}=0$ one obtains from equation (5):

$$\lim_{q,c\to0} (\Delta R/K_1 c) = Q(\Delta\nu)^2 \qquad (7)$$

i.e. light scattering in the isorefractive solvent arises solely as a result of the chemical composition heterogeneity of the investigated copolymer sample. Taking into account the very weak dependence of the excess Rayleigh ratio on concentration in the isorefractive solvent[15-17], it is possible to use concentrations greater than in the non-isorefractive solvent and hence increase the accuracy, so that the authors of reference 5 claimed that measurements in isorefractive solvent were the most sensitive for the determination of Q for statistical copolymers.

However, in our case we could use only the rough approximations of ν_B and $\Delta\nu$, obtained from equation (6) using values $0.60 \leqslant w_A \leqslant 0.73$ (see Experimental). Computed in this way $\Delta\nu$ is small (i.e. species A and B of Cutinox seem to be almost isorefractive each other, cf. *Table 1*). In these conditions both 'parabola fitting' and 'isorefractive solvent' methods fail and cannot provide any acceptable accuracy of chemical composition heterogeneity estimation. For example, $13\,700 \lesssim Q \lesssim 252\,000$ is obtained from equation (7) although there is no reason to expect such large heterogeneities for statistical copolymers of investigated type. At this stage we did not attempt to determine accurate Q values, but we were satisfied by the statement that light scattering experiments for three solutions (in acetone, carbon tetrachloride and xylene) differing considerably in their refractive indices, gave equal $\bar{M}_w$ values within experimental error (5%), hence $P\bar{\nu}\Delta\nu \approx Q(\Delta\nu)^2 \approx 0$ can be assumed[13] in equation (5).

Thus, apparent values of all molecular parameters given in *Tables 2* and *3*, obtained for Cutinox solutions by means of conventional light scattering methods developed for homopolymers can be considered to a good approximation as the real values. The only exception is the second virial coefficient $\bar{A}_2$ for Cutinox solution in the isorefractive solvent: as proved[14,17], one has to obtain $\bar{A}_2 \approx 0$ for $\bar{\nu} = 0$ irrespective of the solvent quality.

Small $\bar{A}_2$ values obtained for carbon tetrachloride and xylene solutions are evidence of the bad thermodynamic quality of those two solvents for Cutinox. The theta temperature for the carbon tetrachloride–poly(methyl methacrylate) (PMMA) system was determined[4] to be 300 K. We have obtained for Cutinox in the same solvent $\bar{A}_2 = 0$ at 294 K. We did not attempt to determine exact theta temperature for xylene solutions because of the poor accuracy of the determination of molecular parameters in this system by light scattering due to small value of the increment $\bar{\nu}$. Our conclusion about solvent quality derived from light scattering results is confirmed by viscometry. The plots of η_{sp}/c *versus* c in acetone end xylene at 298 K were linear and the same value of $[\eta]$ was obtained for both solvents. Intrinsic viscosities ($[\eta]$) and Huggins coefficients (k') are given in *Table 1*. Those quantities determine the concentration dependence of polymer solution viscosity $\eta(c)$:

$$\eta(c) = \eta_0(1 + [\eta]c + k'[\eta]^2c^2 + \ldots) \qquad (8)$$

where η_0 is the solvent viscosity.

Both theoretical and experimental results[4,18] prove that for bad solvents values of $k' \gtrsim 0.5$ are obtained, whereas for good solvents $k' \approx 0.25$. Values of k' in *Table 1* show xylene as a bad solvent for Cutinox and acetone as a good one. The same conclusion can be obtained as those derived from $\bar{A}_2$ values.

Conclusions about the negligible influence of the chemical composition heterogeneity of Cutinox on results of light scattering measurements enables quasielastic light scattering data to be treated by usual methods developed for the case of homopolymer solutions. Average translational diffusion constants $\bar{D}_{oz}$ of Cutinox macromolecules at infinite dilution calculated from extrapolated ACF $y(X)$ by means of cumulant method[12] and hydrodynamic radii $\bar{R}_H$ obtained from Stokes–Einstein formula[4] are shown in *Table 3*.

Molecular weight distribution

Autocorrelation functions $y(X)$ obtained experimentally for Cutinox solutions differed considerably from single exponential functions (cf. *Figure 3*) which are expected for the monodisperse polymer sample. This effect, which is usually considered as an evidence of the polydispersity, can be described by the equation:

$$y(X) = A\int_0^\infty w(D)\mathrm{e}^{-DX}\mathrm{d}D \qquad (9)$$

where $w(D)$ is the distribution function of macromolecular diffusion coefficients D, and A is the proportionality constant dependent on experimental conditions[8]. Integral equation (9) has been solved by means of Provencher's constrained regularization method[19,20] in order to obtain the distribution function $w(D)$. Such functions obtained for Cutinox solutions in acetone, carbon tetrachloride and xylene are shown in *Figure 4*. They may be useful for simple comparisons between Cutinox and other similar copolymers.

The molecular weight distribution $w(M)$ can also be obtained from measured $y(X)$ functions when the following integral equation is solved:

$$y(X) = \frac{A}{\bar{M}_w}\int_0^\infty w(M)M\mathrm{e}^{-D(M)X}\mathrm{d}M \qquad (10)$$

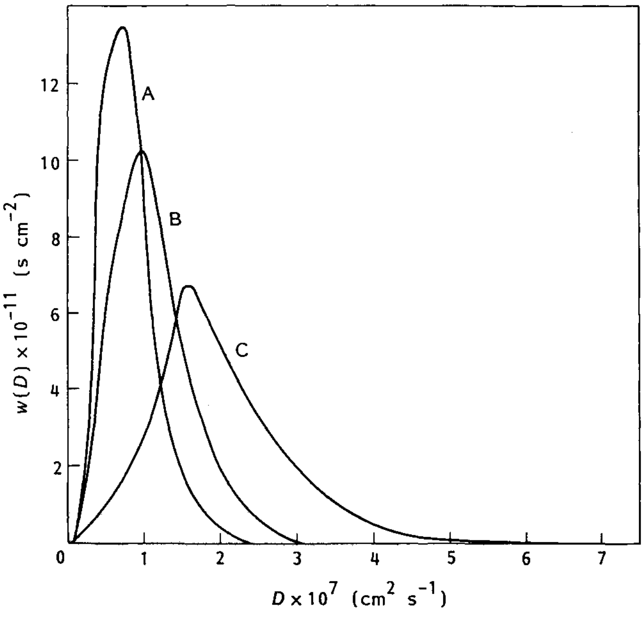

Figure 4 Translational diffusion coefficient distributions $w(D)$ computed from equation (9) for Cutinox macromolecules at infinite dilution: A, in carbon tetrachloride at 294 K; B, in xylene at 298 K; C, in acetone at 298 K

It is only possible however, when the relationship between D and M is known.

We assume that this relation is of the Mark–Houwink–Sakurada type:

$$D=K_D M^{-\gamma_D} \tag{11}$$

As the values of K_D and γ_D for Cutinox solutions are unknown, we assumed $\gamma_D=0.5$ for the Cutinox–carbon tetrachloride system at 294 K. This value of characteristic exponent γ_D is supported both by theory and experiment for the case of flexible chain polymer in theta conditions[18–20]. The proportionality constant K_D was fitted to fulfil the equality $\bar{M}_w^{ELS}=\bar{M}_w^{QLS}$, $\bar{M}_w^{ELS}$ and $\bar{M}_w^{QLS}$ being the weight average molecular weight values obtained from elastic (i.e. static) and quasielastic measurements, respectively. $\bar{M}_w^{ELS}$ is simply the $\bar{M}_w$ value obtained by the Zimm method (*Table 2*) while $\bar{M}_w^{QLS}$ was obtained by solving equation (10) with Provencher's regularization[19], using an approximated value of K_D and $\gamma_D=0.5$ and by computing the $\bar{M}_w$ value obtained from the $w(M)$ function. Similar methods based on K_D fitting are described in the literature[23,24].

As a result of the above procedure the relation:

$$D=0.569\times 10^{-4} M^{-0.5}\ (\mathrm{cm}^2\ \mathrm{s}^{-1}) \tag{12}$$

was obtained for the Cutinox–carbon tetrachloride system at 294 K and the approximated molecular weight distribution function $w(M)$ of the investigated copolymer sample was computed. The result is given in *Figure 5*. The polydispersity index computed from this $w(M)$ function is $\bar{M}_w/\bar{M}_n=2.1(\pm 0.3)$. Concluding, the investigated tributyltin acrylate copolymer sample exhibits rather a broad molecular weight distribution which may be quite accurately described by Schulz–Zimm[4] formula.

Chain rigidity

Assuming that in carbon tetrachloride solution Cutinox forms an ideal chain ($\bar{A}_2=0$) one can compare molecular dimensions of this copolymer with non-perturbed dimensions of PMMA coils[4] exhibiting identical molecular weight $\bar{M}_w$. The radius of gyration ($\bar{R}_{Gz}$) determined experimentally for Cutinox is greater than the $\bar{R}_{Gz}$ value for PMMA. When Cutinox unperturbed molecular dimensions are referred to the radius of gyration of the free vinyl chain R_G^{free} with the same degree of polymerization, the steric factor is obtained:

$$\sigma=\frac{\bar{R}_{Gz}}{R_G^{free}} \tag{13}$$

In order to take into account effects of molar mass polydispersity on σ, values of $\bar{R}_{Gz}$ in equation (13) should be corrected for polydispersity. Assuming $\bar{R}_G \sim M^{0.5}$ at theta conditions and using the Raczek correction procedure[25] we have obtained an $\bar{R}_G^*$ value, that is the radius of gyration for monodisperse sample with $\bar{M}_w$ equal to that of investigated polydisperse one. Replacing in (13) $\bar{R}_{Gz}$ with $\bar{R}_G^*$ the steric factor $\sigma=2.196\pm 0.050$ has been obtained. This value has to be compared with $\sigma=2$ for PMMA and, for example, $\sigma=2.3$ for polystyrene[4]. The same information may be also expressed in terms of $\bar{N}_s$, the degree of polymerization of the statistical segment. $\langle N_s \rangle_w=6.8$ can be computed for the investigated Cutinox sample, while $N_s=6.0$ for PMMA can be found in the literature[4]. Taking the above results into account we conclude that some (although small) increase in chain rigidity is observed for Cutinox compared with PMMA. The increased rigidity could be caused by steric hindrance arising during rotation of tin–organic groups around the main chain bonds.

In a similar way as for the radius of gyration, polydispersity corrections for the hydrodynamic radius $\bar{R}_H$ were taken into account giving $\bar{R}_H^*=26.8(\pm 0.2)$ nm for Cutinox in carbon tetrachloride solution at 294 K.

Both theoretical predictions and experimental results[6,21,22,26,27] give for flexible chain polymers $0.62 \lesssim \bar{R}_H/\bar{R}_G \lesssim 0.82$, depending on the solvent quality. At thete conditions the value $\bar{R}_H/\bar{R}_G \gtrsim 0.75$ is expected. $\bar{R}_H^*/\bar{R}_G^*=0.829\pm 0.012$ for the Cutinox–carbon tetrachloride system fulfils those conditions, and no strong influence of chain rigidity on this parameter can be detected.

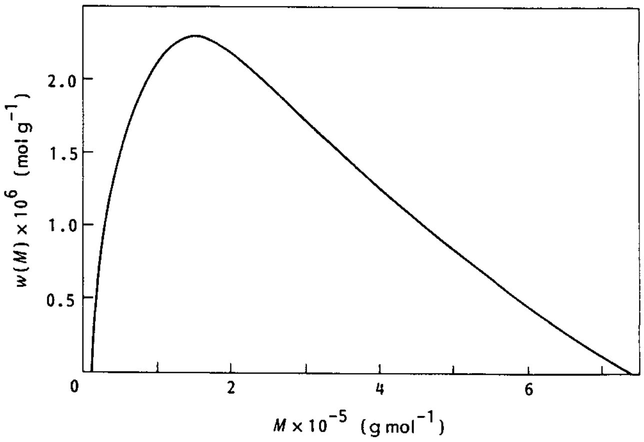

Figure 5 Molecular weight distribution function $w(M)$ for the Cutinox sample, obtained from QLS measurements for dilute solutions in carbon tetrachloride at 294 K. The $w(M)$ values were computed from equation (10) by the constrained regularization method assuming the $D(M)$ relation (15). $\bar{M}_w/\bar{M}_n=2.1$

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