Fractionation and characterization of imidized poly(methyl methacrylate)

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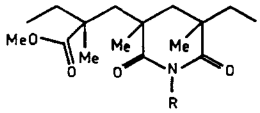
Physical–chemical studies on a sample of NCH_3-imidized poly(methyl methacrylate) (PMMA-I-CH_3) were performed by several characterization techniques. Fractional precipitation by solvent/non-solvent at constant temperature was used, obtaining 12 fractions characterized by different molecular weights. With these fractions of the PMMA-I-CH_3, in the range $2\times10^4<M_w<2\times10^5$, a Mark–Houwink equation was determined. This relationship, in tetrahydrofuran at 30°C, was found to be $[\eta]=2.22\times10^{-4}M_w^{0.66}$. This equation is the starting point for studying the polymer–structure relationships. The determination of various properties, such as viscosity, glass transition temperature, nitrogen content and molecular weights, allowed us to obtain structural information on the copolymer. The imidization degree, evaluated by ^1H n.m.r. spectroscopy, was used to correlate glass transition temperature and polymer structure.

(Keywords: poly(methyl methacrylate); fractionation; characterization)

INTRODUCTION

The methyl methacrylic resins, in consequence of their excellent transparency, weatherability and mechanical properties, are used as decorative materials, car parts and electrical appliances. Moreover these polymers are used as high performance optical fibres in short distance communications, as photosensors, etc. However, their low glass transition temperature (T_g) of about 100°C does not allow their use in fields where high thermal performance is required unless considerable improvement is made to their heat resistance. A typical method for improving the heat resistance of methacrylic resins is imidization[1–6]. For example, imidization of poly(methacrylic acid) and poly(methyl methacrylate) (PMMA) with ammonia or primary amines, in the presence of a solvent[1] or water[2], has been suggested. Methods in which the acrylic polymer is reacted with ammonia or primary amine in an extruder[3], or alternatively in an internally baffled tubular reaction vessel[4], have also been reported. Others have described the continuous preparation of imidized polymers, without the isolation of PMMA, with the addition of a primary amine to the imidization reaction zone[5]. Finally, a method has been designed in which a methacrylic ester polymer and primary or secondary amides are melt reacted at atmospheric pressure[6].

The general structure of the polymer, designated PMMA-I-R, where R corresponds to H, CH_3 or C_6H_5, is as follows:



This work reports studies carried out on the polymer in which R = –CH_3 because of the interesting properties of this polymer in many applications.

EXPERIMENTAL

Reagents

Chlorobenzene, heptane, tetrahydrofuran, ethanol and dioxane, purchased from Fluka AG, were used without further treatment. Methylamine (Fluka AG, purum ⩾97% g.c.) was purified by distillation.

PMMA, Vedril 9 D, was dried at 80°C for 24 h in vacuum before use.

Synthesis of imidized polymer

PMMA-I-CH_3 was prepared by imidization of PMMA solution with methylamine. CH_3NH_2 (56 g) was added over 20 min to a solution of Vedril 9 D (250 g) in chlorobenzene (250 ml), placed in a 1000 ml steel reactor (Buchi BEP-280) under nitrogen atmosphere at 230°C, and the pressure was increased from 0.7 to 3 MPa. These conditions were maintained for 1 h. The reactor was then cooled to 100°C; 250 ml of chlorobenzene were added and the solution was transferred to a three-necked flask equipped with a stirrer. Ethanol (3000 ml) was then added dropwise with constant stirring. The imidized polymer was recovered, washed with ethanol, dried in air for 1 day and under vacuum at 130°C for 2 days. The measured intrinsic viscosity was $0.42\,\mathrm{dl\,g^{-1}}$ in tetrahydrofuran (THF) at 30°C and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) was 2.09.

Fractionation

Fractionation was carried out by precipitation of PMMA-I-CH_3 dissolved in dioxane using heptane as non-solvent. By this method the solvent power was gradually decreased and the polymer was recovered as fractions of decreasing molecular weight.

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A solution (1000 ml) of 5% wt PMMA-I-CH_3 in dioxane was placed in a separation flask and non-solvent added until slight turbidity developed at 30°C. In order to assure equilibrium between the two phases, the cloudy solution was cleared by heating to 70°C; precipitation took place in equilibrium at 30°C. Each fraction was allowed to settle overnight. Every fraction was then separated and dried under vacuum at 80°C. Twelve fractions were separated, corresponding to 98.5% of the dissolved polymer; these are shown in *Table 1*.

Polymer characterization

Intrinsic viscosities were determined on each fraction in THF at 30°C by a Desreux–Bishoff capillary viscometer designed to give kinetic energy corrections lower than 1%. As a consequence, no further corrections were applied. G.p.c. analyses were carried out on THF solutions at 30°C using a Waters 150C instrument equipped with four ultrastyragel columns (10^6, 10^5, 10^4 and 10^3 Å). The universal calibration was produced using monodisperse polystyrene standards in the molecular weight range of 10^4 to 10^6. The Mark–Houwink equation of polystyrene used for the calibration was:

$$[\eta] = 1.41 \times 10^{-4} M^{0.70}$$

Weight average molecular weights were determined by light scattering measurements in THF solutions. A commercial light scattering goniometer (Brookhaven Instrument BI-200SM) was used, fitted with an NEC argon laser, vertically polarized and modulated at 514 nm wavelength. The scattering intensities were measured at five concentrations and 11 angles ($30° \leq \theta \leq 150°$).

The weight average molecular weights were determined by the Zimm plot method, as well as the second virial coefficient and the radius of gyration. All solutions were filtered before use through a 0.45 μm porosity Gelman membrane filter. The instrument was calibrated with filtered toluene using a Rayleigh ratio[7] of $3.2 \times 10^{-5}\ cm^{-1}$. The refractive index increment (dn/dc) was determined with a Brice–Phoenix differential refractometer at 30°C on PMMA-I-CH_3 samples in THF solution. A value of $dn/dc = 0.1150\ ml\ g^{-1}$ was obtained.

Glass transition temperatures (T_gs) of the fractions were determined with a Mettler TA3000 differential calorimeter, using a scanning rate of $20°C\ min^{-1}$. All samples were examined as thin films. They were heated at 200°C for 10 min and quenched to produce a standard glassy state.

Table 1 Fractionation data

Fraction no.	Non-solvent added (ml)	Fractional weight	$[\eta]$ (dl g^{-1})
1	480	0.0467	0.71
2	70	0.0419	0.64
3	20	0.0596	0.54
4	10	0.1249	0.52
5	30	0.1722	0.46
6	50	0.1998	0.36
7	25	0.0562	0.34
8	50	0.1385	0.30
9	50	0.0292	0.26
10	100	0.0275	0.24
11	200	0.0872	0.18
12	[a]	0.0163	0.18
Polymer	–	1.000	0.42

[a] Recovered by evaporation

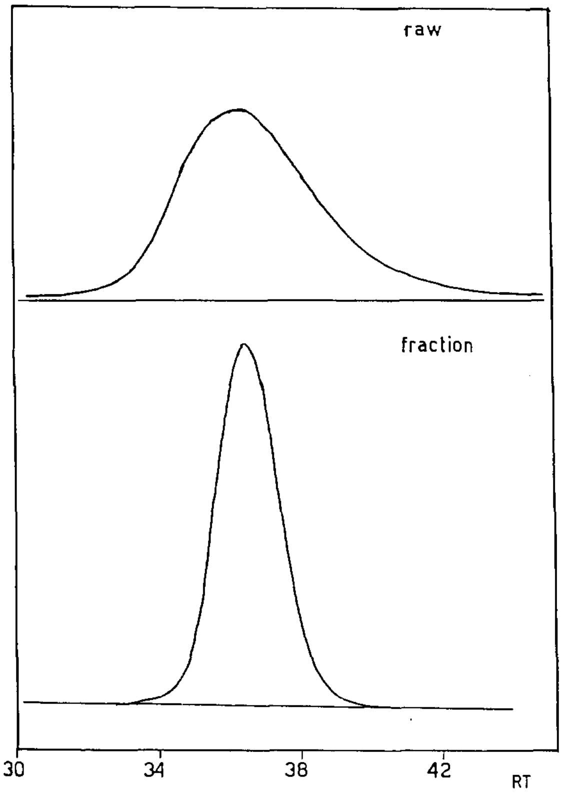

Figure 1 G.p.c. chromatograms of (a) raw PMMA-I-CH_3 and (b) a fraction

The extent of imidization of the fractions was determined by two methods: ^1H n.m.r. spectroscopy and nitrogen content. N.m.r. spectra were measured at room temperature with a Bruker AM 300 spectrometer in dimethylsulfoxide (DMSO)-d_6 solution at 2% w/w. The nitrogen content was also determined by Kjeldahl analysis.

RESULTS AND DISCUSSION

Fractionation

The fractional precipitation of the polymer gave 12 fractions of decreasing molecular weight. *Table 1* shows the different amounts of heptane (non-solvent) added to the solution to separate each fraction. This fractionation method can proceed according to molecular weight or composition or, more generally, by a combination of both. The distribution of the polymer molecules between the two phases in equilibrium may be expressed by the relationship:

$$V'/V = \exp[P(\sigma - Kw)] \qquad (1)$$

where V and V' are the volume fraction of the sample in the solution and in the precipitate phase, respectively, P is the degree of polymerization, σ is the fractionation parameter, while Kw depends on the copolymer composition and solvent interaction.

The fractions were first characterized by intrinsic viscosity measurements, which decreased from 0.71 to 0.18 dl g^{-1}, as seen in *Table 1*, suggesting that the separation was certainly molecular-weight dependent.

G.p.c. chromatograms showed sharp molecular weight distribution for all fractions. As an example, *Figure 1* shows the chromatogram of a fraction compared to the raw polymer. This result supports the previous assumption of fractionation taking place according to molecular weights.

Structural and compositive characterization

The percentage imidization of the polymers was determined by ^{1}H n.m.r. spectroscopy by evaluation of imidic structures and methacrylic monomers in the polymeric chain. Unfortunately, n.m.r. spectra showed broad peaks due to the presence in the chain of conformational and configurational isomers. This prevents a detailed study of comonomeric unit distribution in the polymer, but nevertheless they can be used for composition measurements. From the n.m.r. spectrum of fraction 6, shown in *Figure 2*, three main bands at 3 ppm, due to the NCH_3 group, at 3.6 ppm, due to the OCH_3 group, and at 0.6–2.7 ppm, due to the CH_2 and CH_3 groups, can be observed. Moreover, two weak and broad bands at 12.65 and 7.65 ppm (lower than 2%) were observed; these peaks were assigned to acidic and amidic groups, respectively, which had not reacted to imidic rings.

The imidization degree was consequently calculated according to the relationship:

$$\text{Imidization (\%)} = \frac{(I_{NCH_3}/3)\times 2}{I_{CH_2,CH_3}/5}\times 100 \qquad (2)$$

where I_{NCH_3} and I_{CH_2,CH_3} are the area of the imidic structure and of the polymeric chain, respectively. Although the determination of I_{CH_2,CH_3} could not be very accurate, owing to the broadness of the peak, it represented the skeleton of the whole polymeric chain. All fractions were similar, with little fluctuation from the average value of $85\pm5\%$ in the degree of imidization, as can be seen in *Table 2*.

N.m.r. results were also compared with the nitrogen data from Kjeldahl analysis. The imidization degrees calculated by this method (see *Table 2*) were consistent with each other but not with the n.m.r. data, because of the lower precision of this method. In addition, the peak areas of g.p.c. chromatograms were also reasomably constant ($\sim 9.5\times10^6$) for all fractions. This is in agreement with a constant degree of imidization because these areas depend on the refractive index increments (dn/dc) of the solution, which are strongly influenced by composition.

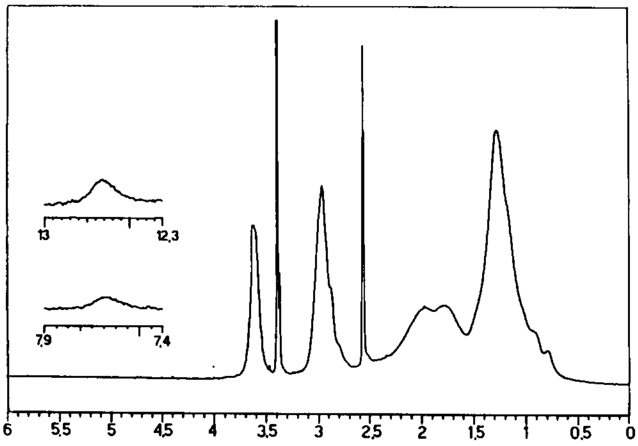

Figure 2 ^{1}H n.m.r. spectrum of PMMA-I-CH_3 of fraction 6

Table 2 Glass transition temperatures and compositive data of fractions

Fraction no.	N (%)	Imidization (%) N.m.r.	Imidization (%) Kjeldahl method	T_g (°C)
1	5.6	86	74	151
2	6.1	84	76	151
3	–	89	–	150
4	5.4	84	68	150
5	5.2	80	66	149
6	5.4	83	68	150
7	–	84	–	150
8	5.9	78	74	–
9	5.6	77	71	150
10	–	92	–	144
11	5.6	85	71	147
Raw	6.2	88	77	150

The T_g values for all the fractions are listed in *Table 2*. In the range of very high molecular weights investigated, T_gs were found to be about 50°C higher than the starting PMMA and practically constant, as further evidence of a homogeneous degree of imidization.

Determination of molecular weights

In order to obtain the Mark–Houwink equation, molecular weights were determinated on some selected fractions by the light scattering method. The excess integrated intensity of the light scattered by a dilute polymer solution is:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w}\left(1+\frac{\langle R_G^2\rangle}{3}\right)+2A_2c \qquad (3)$$

where R_θ is the Rayleigh ratio, R_G^2 the radius of gyration and A_2 the second virial coefficient related to the polymer–solvent interactions. $K=2\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/(\lambda)^4\ N$, and n_0, dn/dc, λ, N and c are, respectively, the refractive index of THF at 30°C, the refractive index increment of the solutions, the wavelength in vacuum of the incident light, the Avogadro number and the polymer concentration[8,9]. Relationship (3), in the limits of zero angle and infinite dilution, gives the weight average molecular weight M_w:

$$\lim_{\substack{\theta\to 0\\ c\to 0}}\left(\frac{Kc}{R_\theta}\right)=\frac{1}{M_w} \qquad (4)$$

A Zimm plot was constructed for each fraction (*Figure 3* shows such a plot for fraction 6). This plot allows a double extrapolation to zero angle and to zero concentration of the intensities scattered by the dilute solutions. Weight average molecular weights calculated by this method are summarized in *Table 3*. These values, with the corresponding intrinsic viscosities, gave the relationship:

$$[\eta]=2.22\times10^{-4}M_w^{0.66} \qquad (5)$$

where the parameters a (=0.66) and K ($=2.22\times10^{-4}$) are the Mark–Houwink coefficients valid for PMMA-I-CH_3 in THF at 30°C.

G.p.c. calibration

Since g.p.c. requires the correlation of the elution volumes (RT) against log(M_w), a calibration curve was

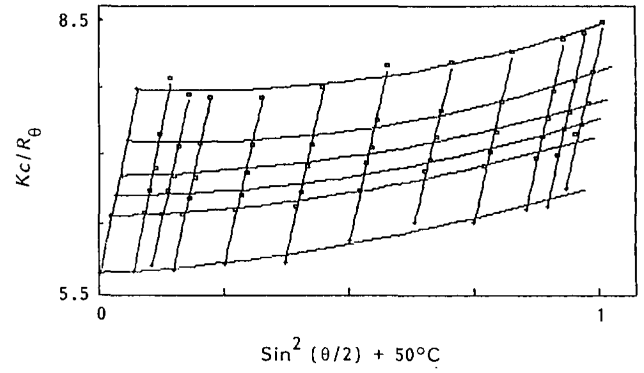

Figure 3 Zimm plot of PMMA-I-CH_3 of fraction 6

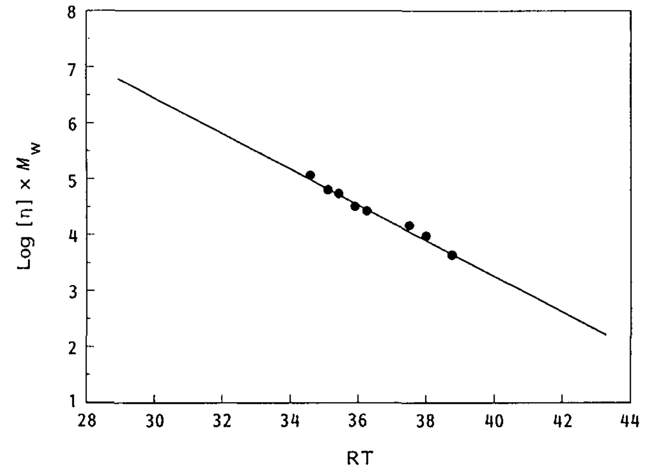

Figure 4 Comparison of the fitting of experimental values of PMMA-I-CH_3 *versus* a universal calibration curve determined with standard polystyrenes

Table 3 Comparison of molecular weights obtained by g.p.c. and light scattering measurements

Fraction no.	M_w(LS)[a] $\times 10^{-3}$	$A_2 \times 10^4$ ($cm^3\,mol\,g^{-2}$)	M_w(g.p.c.)[b] $\times 10^{-3}$	M_w(g.p.c.)[c] $\times 10^{-3}$
1	193	6	184	204
1	150	4.4	156	174
3	–	–	115	166
4	122	8.0	123	138
5	101	8.7	102	114
6	73	11.0	72	81
7	–	–	63	71
8	48	13.0	44	52
9	–	–	37	43
10	39	6.4	31	35
11	24	12.0	23	27
Raw	91	7.0	83	93

[a] LS, light scattering
[b] Molecular weight obtained through g.p.c. calibrated according to equation (5) (PMMA-I-CH_3)
[c] Molecular weight obtained through g.p.c. calibrated according to equation (6) (PMMA)

set up using the universal calibration procedure suggested by Benoit *et al.*[10].

The experimental data obtained for PMMA-I-CH_3 fit well with the universal calibration curve determined with standard polystyrenes ($\log[\eta]M_w = 16.0629 - 0.3204RT$), as can be seen in *Figure 4*. This confirms the possibility of using the reported Mark–Houwink relationship to evaluate molecular weights by g.p.c., normally calibrated with standard polystyrenes.

For comparison, according to the same universal calibration and adopting the Mark–Houwink equation reported for PMMA in THF[11,12]:

$$[\eta] = 1.28 \times 10^{-4} M^{0.69} \qquad (6)$$

molecular weights were determined according to the same RT values, as seen in *Table 3*.

Comparing the molecular weights for all fractions derived by this last calibration, an average increase of about 15% is observed. The difference compares well with the variation of molecular weight, on a monomeric basis, when the $-NCH_3$ imidic cycle is formed in the polymeric chain by reaction between PMMA and methylamine. This observation could be taken as proof that the imidization process does not significantly degrade the initial PMMA chains.

CONCLUSIONS

A Mark–Houwink relationship was obtained for PMMA-I-CH_3, which allows the g.p.c. universal calibration to be used in determinations of molecular weight and molecular weight distribution. The constant values of T_g, nitrogen and N–CH_3, determined by different methods, proved the good homogeneity of the imidization process. Insight into the absence of PMMA degradation during the imidization process was also gained.

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