BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 7, pp. 1415–1419, 1995

0032-3861/95/$10.00+0.00

Glass transition temperature and melting temperature of uniform isotactic and syndiotactic poly(methyl methacrylate)s from 13mer to 50mer

Koichi Ute, Nobuo Miyatake and Koichi Hatada*
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan
(Received 23 August 1994; revised 29 September 1994)

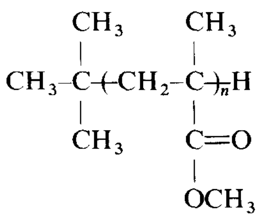
Highly isotactic (it-) and highly syndiotactic (st-) poly(methyl methacrylate)s (PMMAs) were fractionated into the individual homologues (uniform polymers) from the 13mer to the 50mer by means of supercritical fluid chromatography. The glass transition temperature (T_g) and crystalline melting temperature of the uniform PMMA samples were determined by differential scanning calorimetry. The T_g values of the uniform PMMAs were higher than those of the non-uniform PMMAs which are equivalent to the uniform PMMAs in tacticity, number-average molecular weight, and end-group structure. Over the molecular weight range from 1359.6 (13mer) to 5064.0 (50mer), plots of T_g against the reciprocal molecular weight (M^{-1}) are well fitted by a linear relationship: $T_g(°C)=(49.6\pm1.3)-(4.34\pm0.26)\times10^4\,M^{-1}$ for the uniform it-PMMAs and $T_g(°C)=(123.3\pm1.7)-(9.38\pm0.33)\times10^4\,M^{-1}$ for the uniform st-PMMAs. Each uniform it-PMMA with a degree of polymerization (DP)$\geqslant$28 crystallized from its methanol solution by evaporation of the solvent. The reciprocal equilibrium melting temperature (T_m^{-1}) of the crystalline uniform it-PMMAs increased linearly with increasing DP^{-1}. Extrapolation of the linear relationship gave the T_m of it-PMMA at infinite DP as 171.1°C.

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

INTRODUCTION

Most synthetic polymers are inhomogeneous with respect to molecular weight, and thus the structure and properties of such polymers can only be observed as average values. It would be useful for polymer science if 'uniform polymers'[1] were available[2].

Recently, we have succeeded in fractionating highly isotactic ($mm=96\%$) and highly syndiotactic ($rr=92\%$) poly(methyl methacrylate)s (PMMAs) into the individual homologues from the 3mer to the 100mer (molecular weight exceeding 10 000) by means of supercritical fluid chromatography (s.f.c.)[3–6]. The parent PMMAs have a well controlled chain structure:



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}(CH_2{-}\underset{\underset{OCH_3}{C{=}O}}{\overset{CH_3}{C}})_{\mathit{n}}{-}H}$$

A definite molecular weight (M) is known for each of the uniform PMMAs separated by s.f.c.

In the present paper, we report the glass transition and crystalline melting behaviour of the series of stereoregular uniform PMMAs.

The glass transition temperature (T_g) of a polymer increases with increasing molecular weight towards an asymptotic limit; a marked dependence of T_g on molecular weight can usually be seen below a number-average molecular weight, $\bar{M}_n$, of around 10^4. Fox and Flory[7] have shown the relationship between T_g and molecular weight to be given by a simple function of $\bar{M}_n^{-1}$:

$$T_g = T_{g\infty} - K/\bar{M}_n \tag{1}$$

where $T_{g\infty}$ is the T_g of a polymer with infinite molecular weight, and K is a polymer-specific constant. This equation has been found to hold for many polymers including PMMA[8–11]. However, there are experimental results showing that polymer samples with $\bar{M}_n$ lower than about 3000 have T_g higher than predicted by the equation[8,12,13]. It is therefore of interest to examine this effect for our uniform PMMAs with a molecular weight range from 1359.6 (13mer) to 5064.0 (50mer).

Because of the uniformity of molecular weight along with the high stereoregularity, the uniform PMMA samples, particularly the isotactic ones, are expected to be highly crystalline. For a linear polymer homogeneous in molecular weight, a statistical thermodynamic analysis based on a lattice model yields the relation[14]:

$$1/T_m - 1/T_{m\infty} = (R/\Delta H_u)(1+\beta)/DP \tag{2}$$

which represents the dependence of the equilibrium melting temperature (T_m) on the degree of polymerization

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*To whom correspondence should be addressed

(DP). $T_{m\infty}$ is the T_m at infinite chain length, ΔH_u is the heat of fusion per repeating unit, and R is the gas constant. The parameter β can be expressed as follows using the equilibrium (average) crystallite length ζ_e in number of repeating units:

$$\beta=[1-(\zeta_e-1)/DP]^{-1} \qquad (3)$$

We have estimated the $T_{m\infty}$ and ζ_e of isotactic PMMA by applying these equations to the data obtained from differential scanning calorimetry (d.s.c.) of the series of uniform PMMAs.

EXPERIMENTAL

The isotactic (it-) PMMAs (it-A, it-B and it-C in *Table 1*) were prepared by the living polymerization of MMA initiated with t-butylmagnesium bromide[15] in toluene at −78°C and terminated with phenol[16]. The syndiotactic (st-) PMMAs (st-A, st-B, st-C and st-D in *Table 1*) were prepared by the living polymerization of MMA initiated with a t-butyllithium/trialkylaluminium complex[17] in toluene at −93°C and terminated with t-butanol[16].

The uniform PMMA samples from the 13mer to the 50mer were obtained by repeated fractionation of the it- and st-PMMAs (it-A, it-B, st-A, st-B and st-C) using s.f.c. as previously described[4,5]. Each sample of the uniform PMMA showed a single peak in its s.f.c. chromatogram, indicating the uniformity with respect to DP. The DP and M of the uniform PMMAs were determined on the basis of ^{1}H n.m.r. and field desorption mass spectroscopies: $M = DP \times$ the molar mass of a repeating unit ($C_5H_8O_2 = 100.12$) + the molar mass of the end-groups ($t\text{-}C_4H_9 + H = 58.12$) (refs 4 and 5).

D.s.c. measurements were performed on a Rigaku DSC-8230 instrument under nitrogen flow (15 ml min^{-1}). The temperature response of the calorimeter was calibrated with the melting points of high-purity samples of benzophenone and indium. Sample size ranged from 3.9 to 5.1 mg. Just before each T_g measurement, the sample was heated to 150°C in order to remove any residual thermal history and then cooled rapidly to −30°C. The d.s.c. curves for the determination of T_g were recorded at a heating rate of 10°C min^{-1}. The T_g was defined as the intersection of the initial baseline and the sloping portion of the curve, as shown in *Figure 1*, and was determined as an average of three consecutive runs on each sample. Reproducibility of the T_g among the three measurements was within ±0.7°C. The melting temperature determinations were carried out at two heating rates (3 and 10°C min^{-1}) for each sample. The melting temperature observed at 10°C min^{-1} was higher than that observed at 3°C min^{-1} by 1.8°C at most. T_m was evaluated by extrapolating the data obtained at 3 and 10°C min^{-1} to zero heating rate.

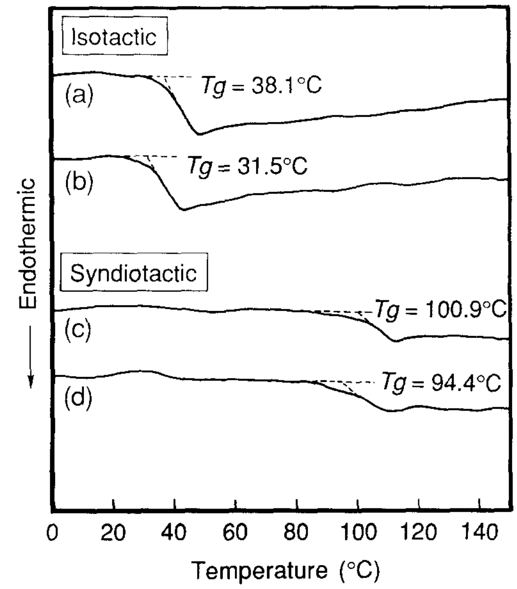

Figure 1 D.s.c. curves of (a) it-41mer, (b) it-B ($\overline{DP}=40.8$), (c) st-41mer and (d) st-C ($\overline{DP}=41.4$) recorded at a heating rate of 10°C min^{-1}

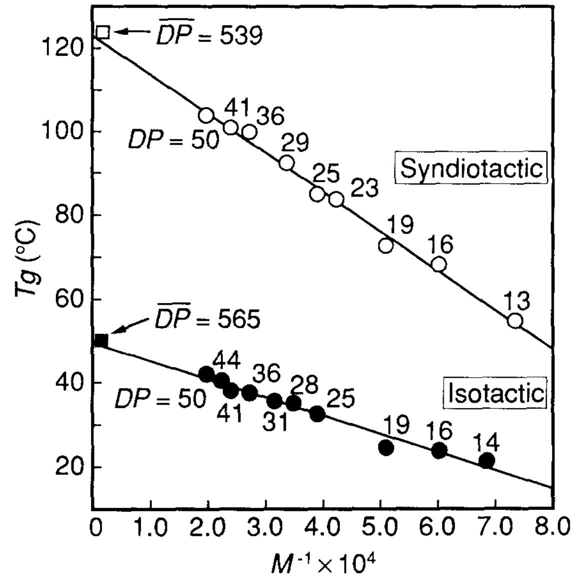

Figure 2 Plots of the T_g of uniform it-PMMA (●) and st-PMMA (○) samples as a function of M^{-1}. The T_g data of it-C ($\overline{DP}=565$) (■) and st-D ($\overline{DP}=539$) (□) are also shown

Table 1 Number-average DP and tacticity of the isotactic and syndiotactic PMMA samples prepared by stereospecific living polymerizations

Sample	$\overline{DP}$[a]	$\bar{M}_w$[b]/$\bar{M}_n$	Tacticity (%) *mm*	*mr*	*rr*
it-A	28.6	1.15	96.1	3.9	0.0
it-B	40.8	1.12	95.9	3.5	0.6
it-C	565[c]	1.24	97	3	0
st-A	23.2	1.08	0.0	8.0	92.0
st-B	26.8	1.09	0.3	7.6	92.1
st-C	41.4	1.05	0.0	7.2	92.8
st-D	539[c]	1.19	0	8	92

[a] Determined from the intensity ratio of the ^{1}H n.m.r. signals due to the end-group ($t\text{-}C_4H_9$) and the monomeric units (CH_3O). The ^{1}H n.m.r. spectra were measured in $C_6D_5NO_2$ at 110°C and 500 MHz

[b] Determined by g.p.c.

[c] Determined by vapour pressure osmometry

RESULTS AND DISCUSSION

Glass transition temperature of uniform it- and st-PMMAs

Figures 1a and *b* show the d.s.c. curves of the uniform it-41mer and the non-uniform it-PMMA with an average

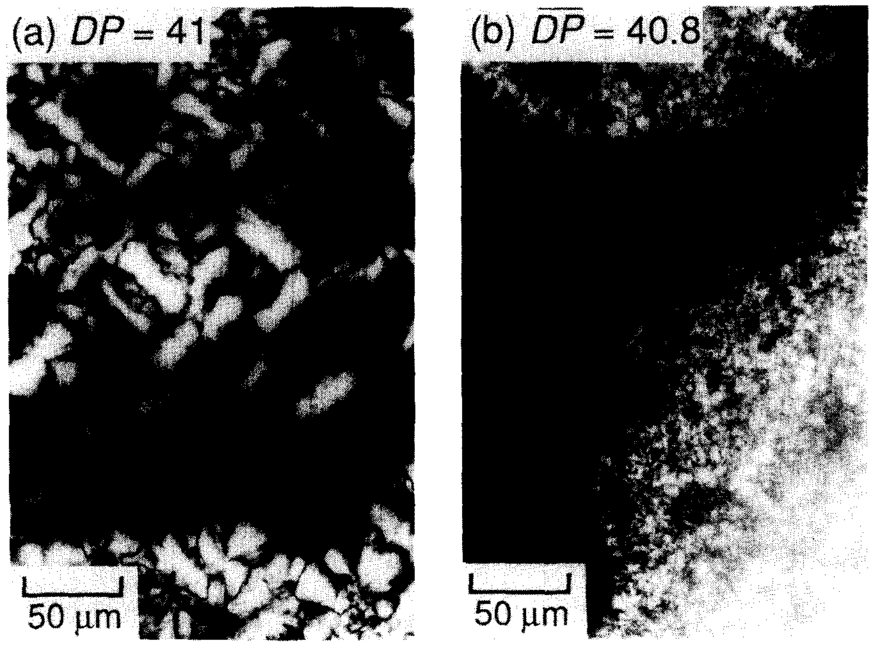

Figure 3 Polarized-light photomicrographs of (a) the it-41mer of MMA and (b) the non-uniform it-PMMA with a $\overline{DP}$ of 40.8 (it-B). Both samples were crystallized by annealing at 90°C for 72 h

DP of 40.8 (it-B in *Table 1*). While the $\overline{DP}$ of it-B is nearly equal to the DP of the 41mer, the T_g of it-B was 6.6°C lower than that of the it-41mer. The lower T_g of the non-uniform PMMA is simply due to the molecular weight distribution existing in the PMMA, though the distribution is rather narrow ($\bar{M}_w/\bar{M}_n = 1.12$). This phenomenon may be caused by the plasticizing effect of the lower DP components included in the non-uniform PMMA. As described in a previous paper[4], it-A also gave a lower T_g (28.0°C) than the uniform it-28mer (34.5°C). A similar effect of molecular weight distribution on lowering T_g was observed between the uniform st-41mer and st-C (*Figures 1c* and *d*).

When the T_gs of the uniform PMMA samples are plotted against the reciprocal molecular weight (M^{-1}), as in *Figure 2*, the data are well represented by a straight line drawn for the it- and st-homologues. From a least-squares analysis one obtains equation (4) for the it-homologues and equation (5) for the st-homologues with standard deviations of 1.25 and 1.55°C, respectively†.

$$T_g = (49.6 \pm 1.3) - (4.34 \pm 0.26) \times 10^4/M \tag{4}$$

$$T_g = (123.3 \pm 1.7) - (9.38 \pm 0.33) \times 10^4/M \tag{5}$$

The slope K for the st-homologues (equation (5)) is over twice as large as that for the it-homologues (equation (4)); it is interesting that the two lines in *Figure 2* cross at $M = 684$ and $T_g = -13.9$°C when extrapolated to the low M side. Although several different $T_{g\infty}$s have been reported for it-PMMA (48.3 (ref. 9), 56.8 (ref. 18) and 60°C (ref. 19)), the present result (equation (4)) supports the value found by Thompson[9]. The $T_{g\infty}$ in equation (5) agrees approximately with that determined for a st-PMMA of similar tacticity (128°C)[11]. Moreover, the T_g data of the non-uniform it- and st-PMMAs having an $\bar{M}_n$ larger than 5×10^4 (it-C and st-D) fit the linear relationships defined by equations (4) and (5) (*Figure 2*). These results indicate that a molecular weight distribution to the extent of $\bar{M}_w/\bar{M}_n = 1.24$ hardly affects T_g in a high molecular weight region ($\bar{M}_n \geqslant 5 \times 10^4$) and that the simple expression given by Fox and Flory (equation (1)) holds for an extensive range of molecular weight ($M \geqslant 1 \times 10^3$).

Beevers and White[8] have reported that the T_gs of atactic PMMA samples with $\bar{M}_n < 5000$ deviated to *higher* temperature than predicted by equation (1). A similar deviation has been found by other authors for poly(α-methylstyrene)[12] and poly(vinyl chloride)[13] with $\bar{M}_n < 3000$. Our results contradict their observations. They determined the T_gs of polymers for samples having a molecular weight distribution (non-uniform polymers). As mentioned above, the T_gs of the non-uniform PMMAs are lower than those of the uniform PMMAs, and deviate to *lower* temperature than expected from the linear T_g *versus* M^{-1} relationship. So far as the T_g of PMMA is concerned, this contradiction seems to be ascribed to the overestimation of the K value in the literature. For example, Beevers and White obtained $K = 2.1 \times 10^5$ for atactic PMMA prepared by radical polymerization[8], and Thompson found $K = 2.95 \times 10^5$ for similar PMMA samples ($rr = 64\%$)[9]. These K values are larger than that found for highly syndiotactic PMMA (equation (5)). The reported[9] K value of highly isotactic PMMA (1.06×10^5) is also more than twice as large as the present result (equation (4)). One possible reason for the overestimation is that the authors[8,9] determined $\bar{M}_n$ of their PMMA samples on the basis of the intrinsic viscosity; the Mark–Houwink equation may not be useful for the correct measurement of $\bar{M}_n$.

Crystalline melting temperature of uniform it-PMMA

Powdery samples of the it-41mer and it-B were capable of crystallizing by annealing at 90°C for 72 h; at this

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† In our previous paper[6] describing the preliminary results of the present work, $T_{g\infty}$ and K for the uniform it-PMMAs were reported to be 51.9°C and 0.52×10^5, respectively, and the corresponding values for the uniform st-PMMAs were 125.7°C and 1.02×10^5, on the basis of the T_g data of the samples from the 19mer to the 50mer

temperature a maximum rate of crystal growth was attained for both samples. Polarized-light photographs of the crystalline materials showed the formation of spherulites (*Figure 3*). The spherulites of the uniform it-41mer were about 35 μm in diameter, and were significantly larger than those of it-B (spherulite diameters less than about 15 μm).

Figure 4 shows the d.s.c. curves of the crystalline samples. A melting endotherm was observed in each curve. The melting temperatures of the it-41mer and it-B were 122.3 and 119.4°C, respectively. A marked difference between the uniform and non-uniform it-PMMAs can be seen in the intensity of the endotherm, which is proportional to the observed heat of fusion per repeating unit (ΔH^*); the ΔH^* of the it-41mer was 2.2 times greater than that of it-B. The difference in ΔH^* should be ascribed to the difference in the degree of crystallinity (w_c), because ΔH^* is related to w_c and ΔH_u by equation (6) and the ΔH_u values of the it-41mer and it-B are believed to be essentially identical.

$$w_c = \Delta H^* / \Delta H_u \tag{6}$$

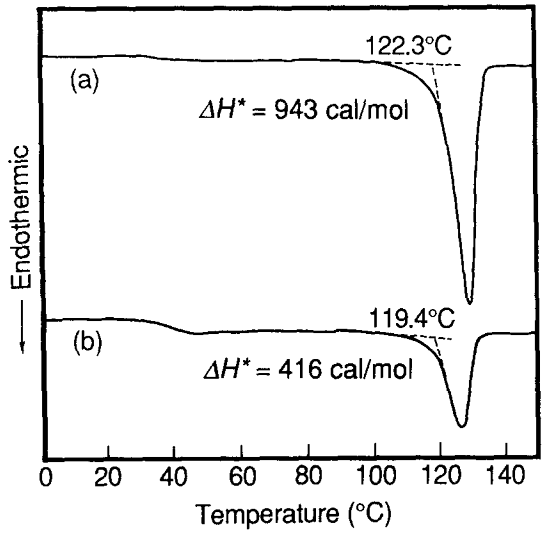

Figure 4 Melting thermograms of (a) it-41mer and (b) it-B recorded at a heating rate of 10°C min^{-1}. Both samples were crystallized by annealing at 90°C for 72 h

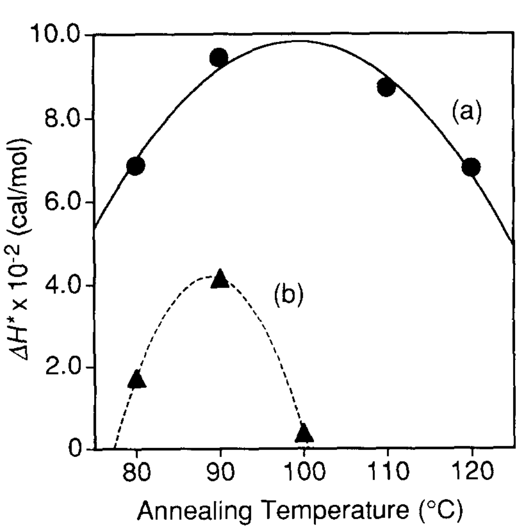

Figure 5 The observed heat of fusion ΔH^* for (a) the it-41mer and (b) it-B crystallized by annealing at various temperatures for 72 h

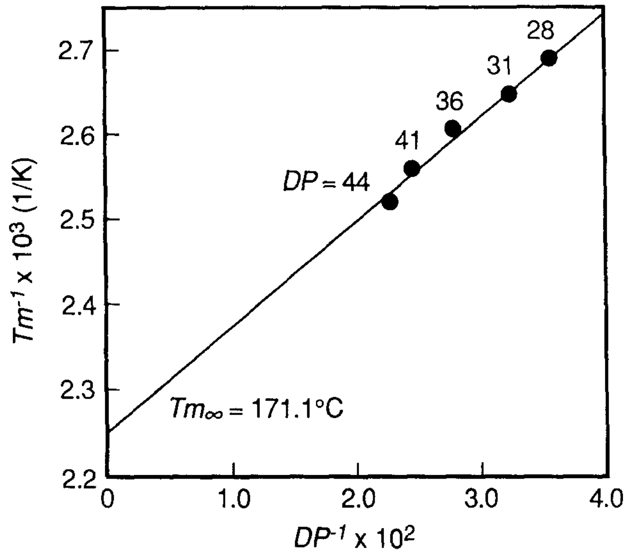

Figure 6 Relationship between T_m^{-1} and DP^{-1} for a series of uniform it-PMMAs. The samples were crystallized from methanol solution by evaporation of the solvent

Table 2 Equilibrium melting temperature $(T_m)^a$, observed heat of fusion per repeating unit $(\Delta H^*)^a$, estimated degree of crystallinity $(w_c)^b$, and equilibrium crystallite length $(\zeta_e)^c$ of the uniform it-PMMAs from the 28mer to the 44mer

DP	T_m (°C)	ΔH^* (kcal mol^{-1})	w_c	ζ_e	ζ_e/DP
28	98.5	1.05	0.88	24.7	0.88
31	104.5	1.14	0.95	27.2	0.88
36	109.6	1.05	0.88	31.5	0.87
41	117.3	1.18	0.98	35.7	0.87
44	124.3	1.11	0.93	38.2	0.87

[a] Determined by extrapolation to zero heating rate

[b] Obtained as $w_c = \Delta H^*/\Delta H_u$ and $\Delta H_u = 1.20$ kcal mol^{-1}. The ΔH_u value is that reported for it-PMMA[20]

[c] Calculated from equation (3) letting $\beta = 6.49$ (see text)

Kusy[20] has documented that the ΔH_u of it-PMMA is 1200 ± 80 cal mol^{-1}. If this value is adopted as the ΔH_u of the it-41mer and it-B, the w_c values of the crystalline samples are estimated to be 0.79 (it-41mer) and 0.35 (it-B). *Figure 5* shows the ΔH^* values of the it-41mer and it-B annealed for 72 h at various temperatures. In comparison with it-B, the it-41mer crystallized at a wider range of annealing temperatures and gave a larger ΔH^* value at any temperature of annealing.

Crystallization of the uniform it-31mer and it-28mer was also attempted by annealing. However, the it-31mer crystallized only slightly ($\Delta H^* = 11$ cal mol^{-1}) after annealing at 80°C for 72 h, and the it-28mer did not crystallize within 72 h at any temperature from 60 to 120°C. Crystallization of the 31mer and 28mer was carried out successfully by slowly evaporating the solvent from methanol solution at room temperature. The 36mer, 41mer and 44mer could be crystallized in a similar manner, and thus further investigations of the equilibrium melting temperature (T_m) were undertaken by use of the samples crystallized by evaporating. The ΔH^* value of the 41mer crystallized by evaporating (1.18×10^3 cal mol^{-1}) was somewhat larger than that of the 41mer crystallized by annealing at 90°C for 72 h (0.94×10^3 cal mol^{-1}).

Figure 6 shows the plots of reciprocal T_m *versus* reciprocal DP, where T_m is given in K and not in °C. The T_m^{-1} of the uniform it-PMMA increased linearly with increasing DP^{-1}, and the relationship is well represented by the following equation:

$$1/T_m = (2.25 \pm 0.012) \times 10^{-3} + (1.24 \pm 0.11) \times 10^{-2}/DP \qquad (7)$$

From the intercept of the straight line, the $T_{m\infty}$ of it-PMMA is given as 171.1°C. The linear relationship between the T_m^{-1} and DP^{-1} of uniform it-PMMAs indicates that $(R/\Delta H_u)(1+\beta)$ in equation (2) should be regarded as constant. Employing the ΔH_u of it-PMMA[20] as previously described, one obtains the value of $\beta = 6.49$ from equations (2) and (7). Then, ζ_e can be calculated from equation (3): the results are summarized in *Table 2*. It should be noted that the equilibrium crystallite length ζ_e amounts to 87–88% of each DP and that the ratio ζ_e/DP agrees fairly well with the degree of crystallinity w_c. The results demonstrate that the crystalline melting behaviour of the uniform it-PMMAs is explained on the basis of the statistical thermodynamic theory[14] for extended-chain (non-folded chain) crystals.

ACKNOWLEDGEMENTS

The authors are grateful to Dr Tatsuki Kitayama and Dr Koji Tashiro of Osaka University for their helpful discussions.

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