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Crystallization and morphology of isotactic poly(methyl methacrylates)

Even Lemieux* and Robert E. Prud'homme

Centre de recherche en sciences et ingénierie des macromolécules (CERSIM), Chemistry Department, Laval University, Québec, Québec, Canada, G1K 7P4

ABSTRACT

Several isotactic poly(methyl methacrylates) (iPMMA), with isotactic triad contents ranging from 46 to 100%, have been investigated after crystallization in the melt at different temperatures by differential scanning calorimetry, polarizing microscopy and small-angle light scattering. It was found that the crystallization of iPMMA, even of samples with high isotactic content, is slow. It never gives high degrees of crystallinity, but nevertheless leads to a spherulitic structure.

INTRODUCTION

Isotactic poly(methyl methacrylate) (iPMMA) is known to crystallize slowly. However, a limited number of studies have investigated its crystallization from the melt (1-3) and, in each case, the conclusions are based on data from a single isotactic sample. To our knowledge, there is only one report in the literature about the morphology of iPMMA. De Boer et al. (1) studied a sample containing 94% of isotactic triads and observed a hexagonal structure after 10 days of crystallization from the melt at 393 K. It evolved, as a function of time, towards a star-shaped structure and, finally, a circular morphology.

It is the purpose of this article to report upon the crystallization and morphology of iPMMA samples whose tacticity ranges from 46 to 100% of isotactic triads. These samples were studied by differential scanning calorimetry (DSC), polarizing microscopy and small-angle laser light scattering (SALS).

EXPERIMENTAL SECTION

Eight iPMMA samples were investigated; they are listed in Table 1 with their triad characteristics (i = isotactic, h = heterotactic, and s = syndiotactic triad fraction), number-average molecular weight (Mn), polydispersity index (Mw/Mn), glass transition (Tg) and melting (Tm) temperatures. Data for a syndiotactic PMMA (SYN-8), which was used in a dilution experiment, are also included in the table. Samples ISO-2, ISO-3, and ISO-4 are commercial samples used without further purification; they exhibit a broad polydispersity index. All remaining samples were kindly supplied by the Laboratory of Macromolecular Chemistry and Organic Synthesis, University of Liège, Belgium. Details about the methods used for the synthesis and the characterization of the samples have been reported recently (4-6) and will not be repeated here.

*Present address: Alcan International Limited, Kingston R & D Centre, Box 8400, Kingston, Ontario, Canada, K7L 5L9

Table 1 : Characterization of the polymers used.

Sample	i/h/s	Mn kg/mole	Mw/Mn	Tg K	Tm* K
ISO-1	100/0/0	38	1.2	328	429
ISO-2	100/0/0	40	7.4	331	427
ISO-3	85/15/0	8	5.6	322	429#
ISO-4	85/15/0	10	6.0	324	428#
ISO-5	63/24/13	97	3.0	348	430
ISO-6	60/25/15	85	3.0	343	428
ISO-7	56/29/15	59	2.8	349	429
ISO-8	46/33/21	40	3.0	355	---
SYN-8	0/24/76	97	1.3	396	---

*) First DSC scan
#) These low molecular weight samples require a short annealing treatment at 393 K in order to crystallize.

Each sample was heated at 10^0/min to above Tm, maintained at a temperature of 453 K for 1 min, and then cooled at a rate of 5^0/min to the crystallization temperature where it was maintained for several days. Some samples were also quenched at 273 K, after being melted at 473 K for 1 min in the DSC.

Photomicrographs were obtained from a Zeiss polarizing microscope on samples which were placed on a microscope slide and heated to 453 K at a rate of 10^0/min on a Mettler hot stage. They were melted for 1 min and cooled at a rate of 3^0/min to a crystallization temperature of 393 K, where they were maintained for at least 30 days unless otherwise stated.

The same samples were studied by SALS, with an apparatus consisting of a He/Ne laser, a polarizer, an analyzer, a shutter, and a type 545 Polaroid camera, using type 57 3000 ASA films. Pictures were taken with the incident light polarized vertically and the scattered light polarized horizontally, defining a so-called Hv pattern. After the usual corrections for the difference in scattering angles in air and in the sample (a value of 1.491 was used for the refractive index of PMMA (7)), the average radius (R) of the spherulites was calculated from the following equation (8):

$$R = 4.1 \lambda / 4 \pi \sin (\theta/2) \qquad (1)$$

where λ is the incident light wavelength in the sample and θ the observed scattering angle after correction for the refraction at the air/sample interface.

RESULTS AND DISCUSSION

Crystallization and fusion

Table 1 gives the Tm values (first scan) of various i-PMMA's. It shows that samples with an isotactic triad content of 56% or larger can crystallize and that, under the experimental conditions used, the Tm values vary little, remaining in the range of 427-430 K. The enthalpies of fusion are small.

The enthalpies of fusion (ΔH) observed under the same preparation conditions, but followed by a 5 min annealing at 373 K, vary from 0 to 9.4 J/g, as illustrated in Figure 1. Annealing for longer times, i.e. 7 days in the 360-380 K range, leads to ΔH values of about 30 J/g for samples of high isotactic triad content. At the same time, the Tm values increase slightly, rising from the 427-430 K range to almost 445 K.

O'Reilly et al. (9) have reported an enthalpy of fusion of 96 J/g for a 100% crystalline iPMMA. With this value, we calculate a degree of crystallinity of 10% for samples annealed for short periods of time, and 28% for samples annealed for several days.

Similarly, for crystallization at 393 K, the enthalpies of fusion of ISO-3 are 10.5 and 22.5 J/g for crystallization times of 15 and 30 days, respectively. However, under these conditions, Tm increases to 447 K (15 days) and to 452 K (30 days), indicating a slow thickening of the crystals in addition to an increase in the degree of crystallinity of the sample.

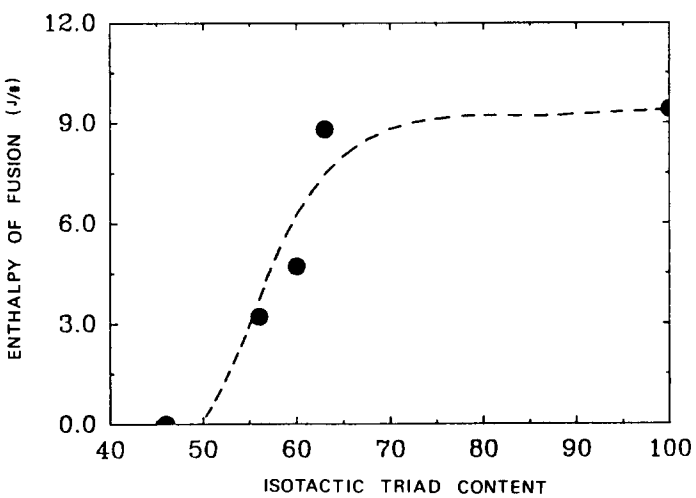

Figure 1 : Enthalpies of fusion of iPMMA's of different isotactic triad contents; samples annealed 5 min at 373 K.

Morphology

Polarized microscopy (Fig. 2) and SALS (Fig. 3) give evidence of the formation of spherulites for iPMMA's with isotactic triad contents greater than 63%, where the samples were subject to the crystallization conditions specified above and long crystallization times. Specifically, a maltese cross pattern can be distinguished in the photomicrographs of Fig. 2 (including that of Fig. 2A, despite the superposition of several spherulitic layers), and a "four-leaf-clover" pattern (8) is apparent from SALS. Average spherulite radii, determined using Eq. 1, range from 34 μm for ISO-1 to 23, 21 and 7 μm, respectively, for ISO-3, ISO-4 and ISO-5 (10). The corresponding value for the ISO-4/SYN-8 (90/10) mixture is 10 μm; this shows the inhibiting effect of syndiotactic PMMA on the crystallization behavior of the isotactic species.

Fig. 2 shows that only the 100% isotactic sample exhibits a volume filling morphology (Fig. 2A). Already at 85% isotacticity (Fig. 2B), we observe black zones indicating non-crystalline regions. At 63% isotacticity (Fig. 2D), only a few spherulites in a sea of amorphous PMMA remain; however, the semi-crystalline structures which do appear clearly present the maltese cross pattern characteristic of well-defined spherulites. These observations are in agreement with the general observation that the crystallization of iPMMA is slow and that it generally leads to low degrees of crystallinity.

It is of interest to note that a similar decrease in the diameter of the spherulites is obtained by either decreasing the isotactic content of the sample (Fig. 2D) or diluting the iPMMA with a small quantity of high syndiotactic content PMMA (Fig. 2C).

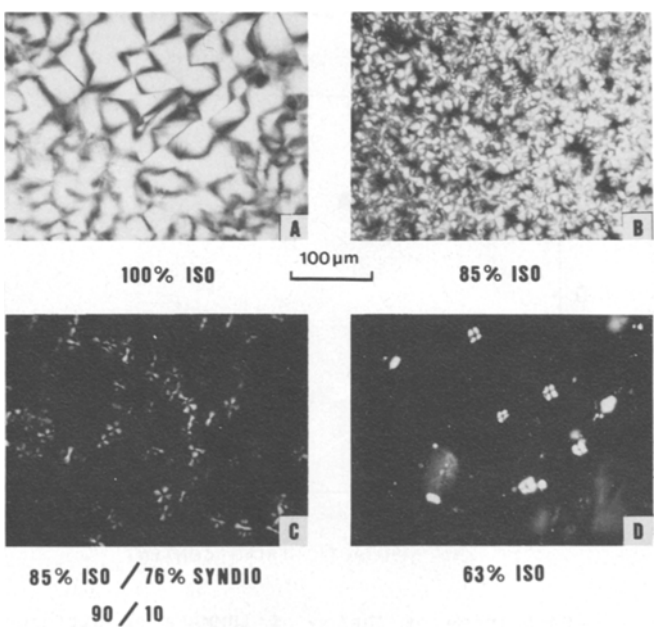

Figure 2. Photomicrographies (between crossed polars) of iPMMA's of different isotactic triad contents: A) 100%, B) 85%, D) 63%, and C) mixture of 90% of ISO-4 and 10% of SYN-8; samples crystallized 30 days at 393 K.

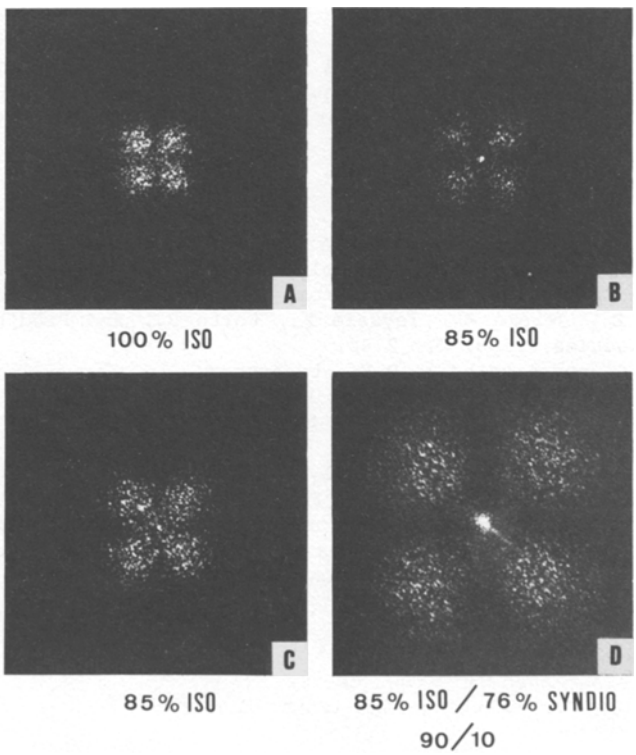

Figure 3. SALS Hv patterns of iPMMA's of different isotactic triad contents: A) 100%, B) 85% (ISO-3), C) 85% (ISO-4), and D) mixture of 90% of ISO-4 and 10% of SYN-8, samples crystallized 30 days at 393 K.

CONCLUSIONS

This study leads to the following conclusions :

1. The crystallization of iPMMA in the melt is slow, even with a nearly monodisperse sample with an isotactic triad content of 100%;

2. Obtaining 25% crystallinity or more requires several weeks of crystallization at an optimum temperature, as well as an isotactic triad content of more than 80%;

3. In all cases, a spherulitic morphology is observed; the spherulites are volume filling at high degrees of isotacticity, but are dispersed in an amorphous matrix at lower isotactic contents;

4. Crystallization is not obtained in samples with an isotactic triad content less than 53%.

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10. The average radius of 7 μm for ISO-5 was measured by polarized microscopy since the Hv SALS pattern could not be observed due to the low spherulitic concentration.

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