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Thermoanalytical study of the methyl methacrylate polymerization under thermal gradient[1]

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Abstract

Cylindrical samples of thermally polymerized methylmethacrylate (MMA) were investigated and the time dependent temperatures at certain positions within the samples were measured during this process. Owing to the polymerization heat evolved, the maximal observed temperature difference within this probe was $\Delta T = 3.5°C$, e.g. the MMA polymerization occurs under a thermal gradient. As a consequence, the maximal difference at the glass transition temperature of the solid PMMA is $\Delta T_g = 1.5°C$, and for samples prepared at a higher temperature gradient (arranged by means of a central "hot wire"), $\Delta T_g = 6°C$. For this cross-sectional inhomogeneity, a difference in the molecular weight distribution for the annealed samples of $\Delta M = 3 \times 10^4$ is proposed.

Keywords: MMA bulk polymerization; Glass transition temperature; Cross-sectional inhomogeneity

1. Introduction

Among many applications of bulk thermally polymerized MMA, at present considerable attention is being payed to its prospective use in polymer fiberoptic production [1]. Several different methods for producing so-called preforms of these fibers, e.g. solid polymerized rods with a given cross-sectional refractive index profile, are already well known. Among them, the recent development and practical implementation of

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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a copolymerization technique for this purpose is very promising [2]. In comparison with previously developed and produced "step index" refractive index profiles, it is possible to accomplish a gradient index (GRIN) as well as other very complicated profiles within the organic polymer materials by such a technique [3].

According to our knowledge, there is a lack of published information and experimental results regarding the influence of the evolved polymerization heat on the polymerization and copolymerization processes and on the homogeneities of the products produced by this method. Therefore, the aim of this work has been to start the experimental investigation of these effects and to show how large degrees of inhomogeneity could be expected, and how these could be regulated and applied.

2. Experimental

2.1. Sample preparation

The MMA monomer was prepared by the following process. The polymerization inhibitor was eliminated by alkaline rinsing, then the residual alkali was removed by washing with distilled water until the pH reached neutrality. Next, the MMA monomer was dried by adding Na_2SO_4, and fractionally distilled in two or three cycles. The success of this final purification step was controlled by means of measuring its refractive index.

The purified MMA monomer was poured into a borosilicate glass ampoule of inner and outer diameters 8 and 10 mm, respectively, with differential thermocouples located according to Fig. 1. This ampoule was placed into the thermostated bath at 50 ± 0.2°C.

2.2. MMA polymerization

It is well known that the thermal conductivity of MMA is very low ($\Lambda = 0.193$ $\mathrm{W\,m^{-1}\,K^{-1}}$) and the polymerization heat is very large ($H = -57.8$ kJ $\mathrm{mol^{-1}}$) [4]. It is to be expected that these two values would influence the thermal polymerization process of the liquid monomer. If the polymerization heat is evolved at a sufficient speed, considerable accumulation of polymerization heat takes place within the central part of such a bulk polymerized sample. With a low thermal conductivity of the surrounding media, large overheating of these parts may occur. In order to quantify this effect for a sample with cylindrical symmetry, an experiment was performed according to Fig. 1.

Three differential thermocouples (copper/constantan wires of 50 μm diameter) were located at the axis of the ampoule (1), near its wall (3), and between these two points (2), respectively. The temperature of the bath, in which this measuring ampoule is immersed, was thermostated at 50 ± 0.2°C.

In a modification of this experiment, a "hot wire" (a platinum wire of 50 μm diameter, by means of which Joule heat is evolved), replaced thermocouple 1, see Fig.1, so

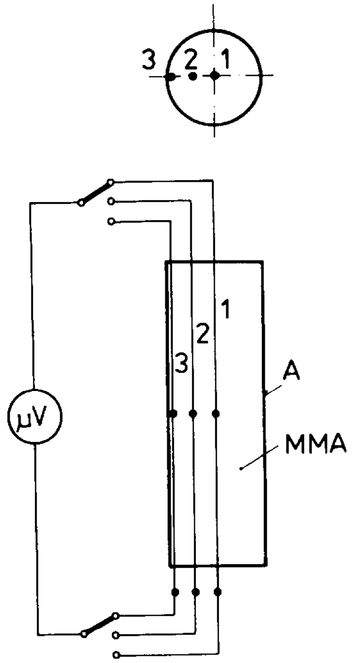

Fig. 1. Basic scheme for the measurement of the polymerizing MMA temperature rise: A, glass ampoule with MMA; 1, 2, 3, differential copper–constantan thermocouples; µV, recording instrument.

as to overheat the MMA monomer along its axis more than in the previous case. Various values of this evolved heat, as well as various bath temperatures, were applied in order to reach the maximal overheating effect. Of course, from a practical point of view, the maximal overheating was limited by the formation of excessive bubbles during MMA polymerization. The maximal and constant superimposed temperature used was 5°C.

2.3. *Thermal analysis*

From solid PMMA rods with the thermal history shown in Fig. 1, and from rods prepared in the thermal gradient arising from the "hot wire" set-up, samples were cut from positions 1–7 (depicted schematically in Fig. 3b).

Differential scanning calorimetry was performed by a DSC-2 (Perkin-Elmer) using block samples 1–7 weighing of 6 ± 2 mg. For the DSC scans, a heating rate of 10 K min^{-1} was used. Certain samples were also measured at rates from 20 to 30 K min^{-1}. In this paper, the T_g is defined as the temperature of the intersection of the baseline and the extrapolated line at the inflexion point of the scan. Before thermal analysis, some samples were annealed at 150°C in a vacuum of 4 Pa for 24 h in order to complete the polymerization.

3. Experimental results and discussion

3.1. Temperature profile of the polymerized MMA

The time-dependent temperatures at the three points of the polymerized MMA sample according to the conditions described in previous sections are depicted in Fig. 2. The central part of the sample is most overheated, as already stated. The maximal temperature difference between the measured places 1 and 3, for our experimental conditions was 3.5°C, and for the "hot wire" methods, 8.5°C.

From the dependence depicted in Fig. 2 and from the well-known theoretical description of this polymerization process, it is evident that the course of the polymerization reaction is characterized by three stages [5].

For the first stage, which is accomplished during the 12.30 h after the beginning of the polymerization process under our experimental conditions, a slow increase in temperature over the whole sample volume is typical. Because the evolution of heat proceeds slowly (with respect to the second stage), the temperature differences between the various volume points are small. This stage reflects the well-known initiation process of the polymerization.

The second stage, which proceeds in our experimental arrangement between 12.30 and 14.00 h, i.e. for approximately one and a half hours, is characterized by a vigorous heat evolution, one order higher than in the previous case, and by clear temperature differences in various radial parts of the sample. From a structural point of view, this stage is characterized by growth of the polymerizing chains.

The third stage, which evolves after 14.00 h, is typical of an equalization of the radial temperature profile within the entire volume. The well-known chain-equalization process takes place during this step.

The second stage is the most important from the point of view of the origin of radial inhomogeneity in the final solid PMMA product. In accordance with Ref. [5], during the polymerization process the distribution of the molecular weight of this polydisper-

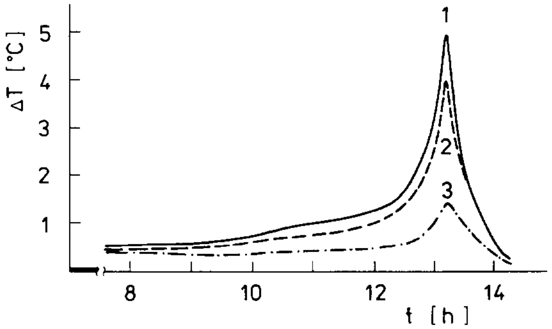

Fig. 2. The dependences of temperature on time during the polymerization of MMA: 1,2,3, dependences numbered according to the location of the thermocouples as in Fig. 1.

sion substance is homogeneous, and is always the same as in the final polymerized products. Of course, these theoretical conclusions are valid only for a constant, equal temperature at every point of this polymerized monomer. If thermal gradients are present, as in our case, the polymerization proceeds under this thermal gradient and the supposed homogeneous equilibrium distribution of the molecular weight is disturbed. From the thermoanalytical point of view, it is not possible to specify a structural model for this new molecular distribution. The most probable interpretation of this process consists of the thermodiffusion of the molecules grown during the second polymerization step, during which chains with a higher number of members are less mobile, and are therefore concentrated at places with higher temperatures, and vice versa. This new distribution of molecular weights also persists in the final, polymerized product and, in such a way, will give rise to the inhomogeneous profile, e.g. an inhomogeneous profile of all the physical parameters.

3.2. Differential scanning calorimetry

The DSC thermograms in the glass transition regions of samples 1–7 (for the "hot wire" case) are presented in Fig. 3. Two of its characteristics are considered most significant.

3.2.1. The shift of the glass transition temperature T_g

To our knowledge, the T_g shift arising in the bulk of thermally polymerized PMMA probes has not yet been published. These shifts are evident from Fig. 3. The central part of the sample cross-section profile is characterized by a higher glass transition temperature and vice versa. For the case depicted in Fig. 3, the maximal shift is $\Delta T_g = 6°C$. This characteristic T_g profile also persists after annealing of all the samples. After this thermal treatment, the polymerization reaction is complete, and some amount of unpolymerized monomer is probably removed, which is reflected in the higher T_g values of the annealed samples. The graphical dependences of the T_g shifts for all the samples studied are presented in Fig. 4.

In order to eliminate methodical and various experimental factors from our DSC measurements, their conditions (sample weights and positions in the measuring head, shape, measuring atmosphere, etc.) were practically the same for all samples. Despite this, other factors which strongly influence the measured T_g values are well known. Among the most important are the unpolymerized monomer, solvents and water [4]. Obviously, the appropriate annealing completed the polymerization and removed the impurities mentioned. For an MMA, which is thermally polymerized, an annealing for 24 h at 110°C and a vacuum of 0.2 Torr is probably sufficient to remove the mentioned factors [2], and therefore practically the same annealing conditions were also used in our experiments (see Fig. 4). After eliminating all possible faults from our T_g evaluation, we come to the conclusion that the observed T_g shifts reflect the structural changes in PMMA, and that they are dependent on the thermal gradients within the bulk of the polymerized monomer as well as on the annealing conditions.

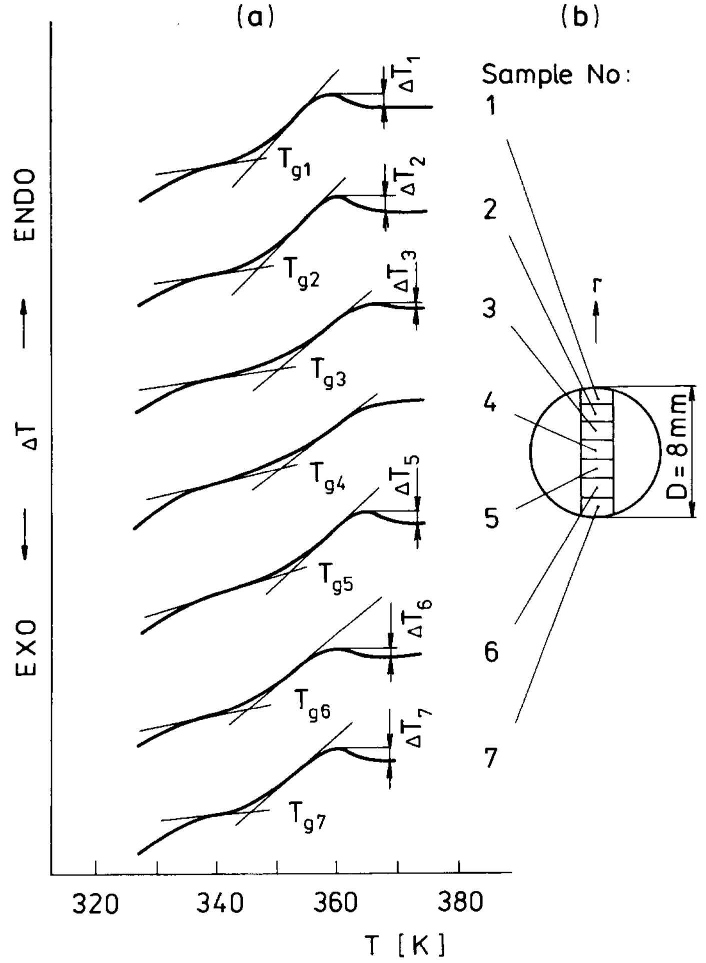

Fig. 3. DSC scans of the as-prepared PMMA for the “hot wire” method (a) and location of the carved samples (1–7) within the PMMA cross-section (b).

The dependence of T_g on molecular weight, studied by means of both γ-irradiation and by free radical polymerization, was published in Ref. [6]. The relationship between the glass transition temperature and molecular weight in this work was established experimentally, and was theoretically best-fitted by the expression of Gibbs [7]. If one accepts our interpretation about nonequilibrium distribution of molecular weights arising in the temperature gradient of the polymerizing monomer, the maximal difference of molecular weights (between the annealed samples 1 and 4, Fig. 4, dependence c) in relation to the results of Ref. [6] is $\Delta M = 3 \times 10^4$.

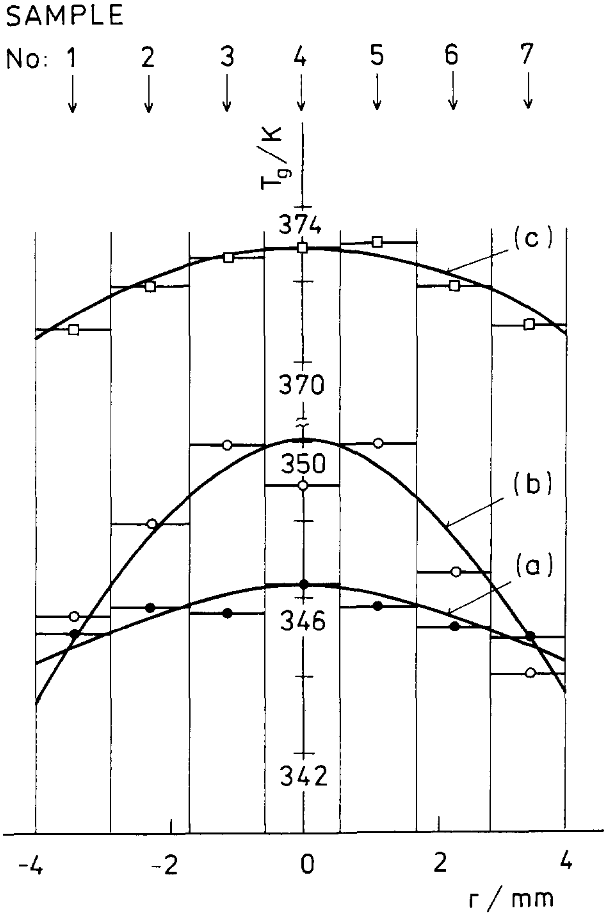

Fig. 4. Radial dependence of the T_g in the cylindrical bulk of PMMA (samples numbers according to Fig. 3): (a) sample prepared by the "hot wire" method (as-prepared), measured values depicted by ●; (b) spontaneous heat removal, measured values depicted by ○ ; (c) annealed samples (a) at 150°C for 24 h at 4 Pa, measured values depicted by □.

3.2.2. The enthalpy relaxation

From the thermoanalytical point of view, the relaxation of this structure appears as a peak in the glass transition region, and according to Wunderlich is interpreted as an enthalpy relaxation. The shape of this peak depends on the cooling rate of the amorphous substance [8]. This relaxation peak with given heights $\Delta T_1 - \Delta T_7$ is centrosymmetric in our case (Fig. 3), and reaches its maximal value at the sample wall. Under our experimental conditions, these peaks are observable only for the samples prepared by the "hot wire" principle and are completely removed after temperature annealing. Their presence probably reflects the existence of unpolymerized monomer in the polymer structure.

4. Conclusion

To summarize our experimental observations, we conclude, that all the studied bulk thermally polymerized PMMA samples were radially inhomogeneous. In order to test the radial symmetricity of this inhomogeneity, samples from the whole profile as well as from various ampoule positions along the length were investigated thermoanalytically. Within experimental error, the symmetry of the results obtained was good.

The glass transition temperature and the relaxation peaks arising at the glass transition region change considerably through the cross-section. The rough radial dependence of T_g shows an exponential-like profile. According to the published results, the observed T_g shift is accompanied by differences in the molecular weight. Therefore, other physical parameters are also radially inhomogeneous. The optical density is particularly interesting because of the possibility of producing polymer optical preforms and fibers according to this principle.

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References

[1] T. Ishigure, A. Horbige, E. Nihei and Y. Koike, Electron. Lett., 30 (1994) 1171.
[2] T. Ishigure, E. Nihei and Y. Koike, Appl. Optics, 33 (1994) 4261.
[3] Y. Koike, Polymer, 32 (1991) 1737.
[4] J. Brandrup and E.H. Immergut, Polymer Handbook, 3rd edn., John Wiley & Sons, New York, 1989.
[5] W. Holzmüller and K. Altenburg, Physik der Kunststoffe, (tschechische Auflage), SNTL, Prag, 1961, p. 44.
[6] R.P. Kusy, M.J. Katz and D.T. Turner, Thermochim. Acta, 26 (1978) 415.
[7] J.H. Gibbs, J. Chem. Phys., 25 (1956) 185.
[8] G. Hentze, Thermochim. Acta, 15 (1976) 139.