Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

ELSEVIER

Polymer 45 (2004) 2813–2816

polymer

www.elsevier.com/locate/polymer

Glass transition and structural relaxation of nano-particle aggregates of atactic poly(methyl methacrylate) formed in microemulsions

Liang Li[a], Bing Li[a], Jinglu Chen[a], Dongshan Zhou[a], Gi Xue[a,*], Xiaoning Liu[b]

[a]*Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Chemistry Building, Nanjing 210093, China*
[b]*College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China*

Received 30 August 2003; received in revised form 2 February 2004; accepted 12 February 2004

Abstract

Atactic poly(methyl methacrylate) (*a*-PMMA) nano-particles were prepared in three-component microemulsions using the cationic surfactant cetyltrimethylammonium bromide. To analyze the thermal history, the sub-T_g annealed sample was subsequently measured at a faster heating rate. The *a*-PMMA prepared in microemulsions shows higher glass transition and higher structural relaxation than those of bulk sample of the same tacticity and the same molecular weight. When the annealing time is longer, additional enthalpy relaxation and glass transition were observed at higher temperatures due to partial self-aggregation of *a*-PMMA chains, which was proved by spectroscopic studies.

Keywords: Atactic poly(methyl methacrylate); Microemulsion; Glass transition

1. Introduction

It has been reported that polymerizations of methyl methacrylate in ternary oil-in water microemulsions using cetyltrimethylammonium bromide surfactant could produce latex particles having weight average diameters of 17–41 nm [1], and that single-chain or pauci-chain polymer particles can be generated conveniently by free-radical polymerization of oil-soluble monomers in three-component (monomer, water, and surfactant) microemulsions [1–6]. However, there is only very little description of the conformation and thermal properties of such prepared polymer nano-particles [1,4–6].

For semicrystallizable polymers, such as isotactic polystyrene, poly(ethylene terephthalate), and syndiotactic poly(methyl methacrylate), the crystallization process usually occurs while annealing the sample between its glass transition temperature and melting temperature [7–11]. For syndiotactic poly(methyl methacrylate), self-aggregation was observed in solutions of toluene [12]. However, for *a*-PMMA with its low tacticity, it is difficult to form some ordered structure either in solution or in the solid state [12,13]. There are few reports about the formation of ordered structures of atactic polymer nano-particles [14].

Structural relaxation is the process by which amorphous materials in the glassy state approach a state of thermodynamic equilibrium. This process is detected through the time evolution of thermodynamic properties such as specific volume or enthalpy, as well as mechanical or dielectric properties. Differential scanning calorimetry (DSC) has revealed enthalpy relaxations occurring near T_g in glassy polymers aged after a wide variety of treatments. To analyze the thermal history, the slow cooled sample is subsequently measured at a faster heating rate. Wunderlich pointed out that sub-T_g annealing or any difference between heating and cooling rates leads to hysteresis effects that show up as endotherms or exotherms in the DSC or DTA traces [14]. Petrie et al. demonstrated that the magnitude of the DSC endothermic peak at T_g provided a quantitative measure of the enthalpy relaxation which had occurred during prior annealing at temperatures somewhat below T_g [15,16]. Matsuoka has suggested that dilation under tensile stress increases the enthalpy of the glass, reducing the relaxation

---

* Corresponding author. Tel.: +86-25-83592569; fax: +86-25-83317761.
E-mail address: xuegi@nju.edu.cn (G. Xue).

0032-3861/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.02.021

time and, therefore, increasing the rate of enthalpy relaxation during annealing [17].

In this work, the structural relaxation behavior of *a*-PMMA nano-particles were studied by DSC measurement and found to be different from that of bulk sample. We report here partial aggregation during thermal treatments of the nano-particle *a*-PMMA formed in microemulsions.

2. Experimental

2.1. Sample preparation

Cetyltrimethylammonium bromide (CTAB) and potassium persulfate (KPS), from Beijing Chemical Plant, were purified by recrystallization. Methyl methacrylate (MMA) from Shanghai Chemical Co. was vacuum distilled before polymerization. Water was deionized and distilled.

MMA was polymerized in microemulsions following W. T. Ford's method [1]. For the purpose of comparison, a bulk *a*-PMMA sample was prepared by dissolving the *a*-PMMA particles formed in microemulsion polymerization in chloroform, and then re-precipitated by adding ethanol.

2.2. Characterization

Transmission electron microscopy (TEM) was performed using a JEOL Model JEM-200CX instrument. Polymer molecular weight was measured on Waters 410 gel permeation chromatography instrument at 40 °C, using polystyrene calibration standards. The solvent is THF. The tacticities of the polymer were determined in deuterated chloroform by means of 500 MHz proton NMR spectroscopy (Bruker AM-500). Differential scanning calorimetry (DSC) measurements were carried out in Perkin–Elmer DSC model 7 system at a heating rate of 20 °C min^{-1}. Temperature calibration was performed using indium as a standard. All the thermal annealing processes for DSC scans were carried out in the calorimeter. Infrared spectra were taken using a Bruker IFS66V FT-IR spectrometer. All of the spectra were taken with 4 cm^{-1} resolution.

3. Results and discussion

The weight average molecular weight (M_w) of the microemulsion polymerized *a*-PMMA is 2.1×10^6 by GPC measurement. It is found that diameters of the most micro-latexes are in the range of 20–40 nm by TEM observations. The tacticities of our *a*-PMMA from NMR triad analysis are as follows: syndiotactic (rr), 58%; heterotactic (mr), 34%; isotactic (mm), 8%. These data are similar to those reported in literature [1,18]. The average number of polymer chains per particle for the PMMA sample, calculated according to the method proposed by Ford and co-workers [1], equals to about 1.4, which is consistence with the results of PMMA obtained by microemulsion [1] and indicates that the sample has less chain interpenetrating than ordinary bulk polymerized PMMA sample. The conformation of *a*-PMMA may be more complicated and will show some unique physical behaviors.

Fig. 1(A) shows the DSC thermograms of heating scan at 20 °C min^{-1} for the nascent microemulsion *a*-PMMA. The inset schematically shows that the *a*-PMMA chain is confined in a nano-spheric emulsion. There are mixed exothermic and endothermic peaks near the glass transition region of the heating scan of Fig. 1(A) due to the release of internal stress of the confined chains formed in microemulsion cells. Fig. 1(B) shows the second scan of microemulsion *a*-PMMA, in which a glass transition at 126 °C can be observed. Fig. 1(C) shows the DSC scan of a bulk *a*-PMMA, which was re-precipitated microemulsion *a*-PMMA. A slightly lower glass transition at 124.8 °C was observed in Fig. 1(C). More significant differences in T_g between these samples were observed after sub-T_g annealing and the results will be shown below.

The curves in Fig. 2(A) and (B) correspond to the DSC heating thermograms for *a*-PMMA particles formed in microemulsions and the bulk film prepared by solution-casting from the *a*-PMMA particles, respectively. The samples had been annealed at 120 °C for 1 h before thermal analysis. Typical sub-T_g endothermic peaks are observed in these pre-treated samples. It shows common relaxation behavior of amorphous polymers as studied by Hodge et al. [19]. Fig. 2(A) shows a stronger endothermic peak than that in Fig. 2(B), indicating a higher enthalpy relaxation for the *a*-PMMA prepared in microemulsions.

The glass transition temperatures of the single chain polymer differ from those of the ordinary multi-chain

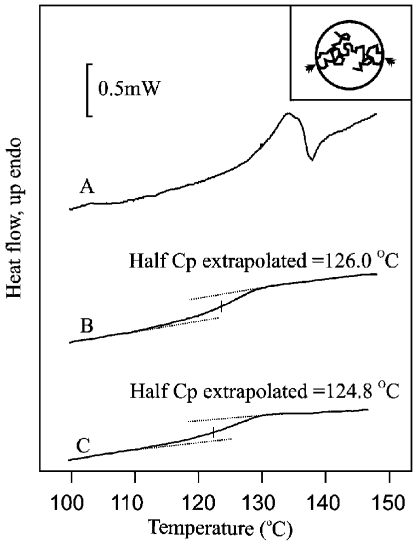

Fig. 1. DSC thermograms of heating scan at 20 °C min^{-1}: (A) first scan of microemulsion *a*-PMMA, (B) second scan of microemulsion *a*-PMMA and (C) DSC scan of bulk *a*-PMMA. Note: the inset schematically shows that the *a*-PMMA chain is confined in a nano-spheric emulsion.

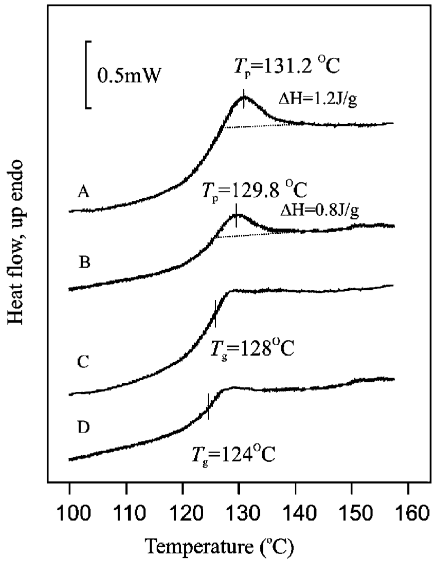

Fig. 2. DSC heating curves (at 20 °C min$^{7-1}$) after annealing the samples at 120 °C for 1 h: (A) first scan of microemulsion *a*-PMMA, (B) first scan of bulk *a*-PMMA, (C) second scan of microemulsion *a*-PMMA and (D) second scan of bulk *a*-PMMA.

polymers. It has been found that the T_g of microemulsion polymerized PS is a few degrees higher than that of ordinary PS [8,9]. The lower curves in Fig. 2 shows the second heating DSC scan of *a*-PMMA samples. The T_g of the *a*-PMMA formed in microemulsion is found to be 128 °C (Fig. 2(C)). The T_g value of the re-precipitated *a*-PMMA from chloroform is 124 °C (Fig. 2(D)), which is 4 °C lower than that of virgin *a*-PMMA. This implies that the confined conformation of *a*-PMMA resulted in its high T_g after thermal treatment.

Fig. 3(A) shows the DSC heating curves for the virgin *a*-PMMA polymerized in microemulsions after annealing at 120 °C for 3 h. It is found that one additional endothermic peak appears at 145 °C following the major enthalpy relaxation peak near the glass transition of *a*-PMMA prepared in microemulsions. This new endothermic peak might originate from the enthalpy relaxation of another amorphous region formed during the heat treatment. Fig. 3(a) shows the second heating curve for the sample. One can see two glass transitions at 125 and 143 °C, with ΔC_p of 0.2 and 0.08 J g^{-1} °C^{-1}, respectively. Commercial samples of PMMA such as a cell cast sheet typically have a T_g of about 105 °C. The highest T_g of a commercial PMMA is about 115 °C [1]. The PMMA produced in the microemulsions or emulsions has T_g of about 125 °C [1]. It is interesting that proper heat-treatment for *a*-PMMA formed in microemulsions would result in two T_g regions after long time sub-T_g annealing. We propose that the partial self-aggregation of *a*-PMMA segments in nano-particles during heat treatment introduced a hard amorphous region, where the cooperative movement of atoms was restricted. For comparison, the DSC thermograms of the bulk *a*-PMMA are shown in Fig. 3(B) and (b). There is no endothermic peak appearing at about 144 °C in Fig. 3(B) and only one glass transition 125 °C in Fig. 3(b). This result indicates that partially aggregated structure can only be formed in microemulsion polymerized PMMA nano-particles after annealing. Solution re-precipitated *a*-PMMA from chloroform results in the destruction of the isolated single-chain particle and the formation of interpenetrating multi-chain systems, and no partially ordered structure can be formed after annealing this sample, although it has the same molecular weight and the same tacticity as the virgin nano-particles formed in microemulsions.

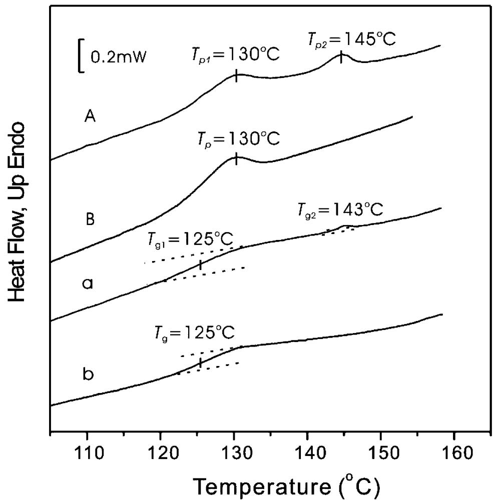

Fig. 3. DSC thermograms of microemulsion polymerized *a*-PMMA after annealing at 120 °C for 3 h: (A) the heating curve at 20 °C min^{-1} of the firs scan and (a) the second scan at 20 °C min^{-1} of the sample in (A). DSC thermograms of re-precipitated *a*-PMMA after annealing at 120 °C for 3 h: (B) the heating curve at 20 °C min^{-1} of the first scan and (b) the second scan at 20 °C min^{-1} of sample in (B).

Stereoregular PMMAs have received considerable attention during the past 20 years. One of the most interesting features of these systems is the ability to form helix structures and especially double-stranded helix structures, which are often encountered in biological systems but more rarely in synthetic polymers [20–22]. Self-aggregation of *s*-PMMA has been studied extensively by means of ^{1}H NMR, infrared spectroscopy, light scattering, osmometry, viscosity and small angle neutron scattering [20–22]. As to atactic PMMA, because of its low tacticity, no association was detected in solutions of *a*-PMMA in bromobenzene and toluene [20–22]. Fluorescence anisotropy study of the pyrene labeled PMMA showed that below the gelation temperature, *s*-PMMA/toluene solution forms rigid gel and the fluorescence of the probe shows anisotropy [20–22]. A dilute solution of *s*-PMMA shows no fluorescence anisotropy, neither do solutions of labeled *a*-PMMA at any concentration in the same temperature region. This indicated that no gelation was occurred in *a*-PMMA at any concentration and the system was a homogenous solution. NMR study also concluded that no association was detected in solutions of *a*-PMMA in bromobenzene [20–22]. Very recently, it was shown that in semidilute solutions (acetone, CCl_4, acetonitrile) *a*-PMMA forms associated structures due to the mutual interactions of short *i*- and *s*-sequences (stereocomplex type) [23]. These structures preserved also in solid films cast from acetone solutions [24,25]. The changes in molecular conformation of PMMA particles can be followed by infrared spectroscopy [20–22]. Fig. 4 shows IR spectra recorded for the virgin *a*-PMMA particles formed in microemulsions (4A) and for the re-precipitated polymer (4B). Fig. 4(C) and (D) showed IR spectra of microemulsion *a*-PMMA after annealing for 1 and 3 h, respectively. IR spectroscopy can be used to study the conformation of PMMA since the 1800–1000 cm^{-1} absorption range is known to be ally conformation sensitive [19–22]. In this range intensive absorption bands can be observed which are assigned to the ν(C=O) vibration. In the case of the single-chain *a*-PMMA particle, the nearest-neighbor segments in space are necessarily segments of the same chain; these may be located remotely along the contour of the chain but are placed in close proximity by coiling. Annealing near its glass transition temperature for sufficient long time will increase the interactions between side-groups. In Fig. 4(D), the carbonyl band became broader and shifted to higher wave numbers (1739 cm^{-1}), which is characteristic of self-aggregation of *s*-PMMA due to the interactions between ester groups from the interacting *s*-sequences [20–23]. This result indicated that partially ordered structures formed after annealing of *a*-PMMA sample near its T_g. The kinetics of the enthalpic relaxation process seems to be different in each amorphous region due to the different mobility of the chain segments. The mobility in the self-aggregated amorphous region is more constrained than in that in amorphous region un-associated.

In the small volume of a latex particle formed in a microemulsion, the polymer chain must have more gauche conformations than in its unperturbed state, especially near the surface of the particle, so that the path of its random walk turns back into the particle [26,27]. Therefore, the polymer formed in a microemulsion is conformationally restricted. After annealing near the glass transition temperature of PMMA, the adjustment of conformation of PMMA in nano-particle to some kind of partially ordered state is possible.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (No. 50133010, 90103036 and 20374027) and the State Key Laboratory of Polymer Materials for Adsorption and Separation, Nankai University.

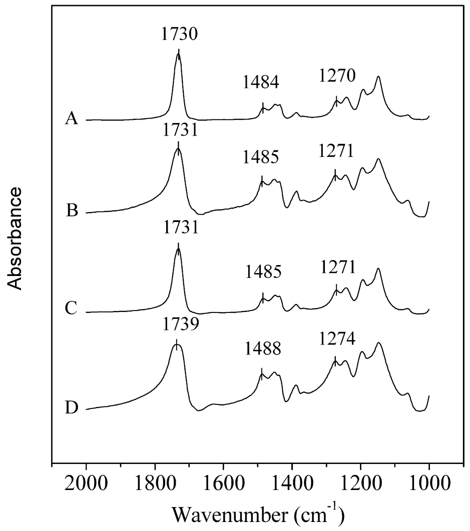

Fig. 4. IR spectra of *a*-PMMA: (A) virgin microemulsion polymerized *a*-PMMA, (B) re-precipitated *a*-PMMA from chloroform, (C) microemulsion polymerized *a*-PMMA after annealing at 120 °C for 1 h and (D) microemulsion polymerized *a*-PMMA after annealing at 120 °C for 3 h.

References

[1] Pilcher SC, Ford WT. Macromolecules 1998;31:3454.
[2] Antonietti M, Lohmann S, Niel VC. Macromolecules 1992;25:1139.
[3] Full AP, Puig JE, Gron LU, Kaler EW, Minter JR, Texter J. Macromolecules 1992;25:5157.
[4] Antonietti M, Basten R, Grohn F. Langmuir 1994;10:2488.
[5] Gan LM, Lee KC, Chew CH, Ng SC. Langmuir 1995;11:449.
[6] Qian R, Wu L, Shen D, Napper DH, Mann RA, Sangster DF. Macromolecules 1993;26:2950.
[7] Ngai KL. Eur Phys J E 2002;8:225.
[8] Kawana S, Jones RAL. Eur Phys J E 2003;10:223.
[9] Reiter G, Gennes de PG. Eur Phys J E 2001;6:25.
[10] Ellison CJ, Kim SD, Hall DB, Torkelson JM. Eur Phys J E 2002;8:155.
[11] Bernazzani P, Simon SL, Plazek DJ, Ngai KL. Eur Phys J E 2002;8:201.
[12] Spevacek J, Schneider B, Dybal J, Stokr J, Baldrian J. J Polym Sci, Polym Phys Ed 1984;22:617.
[13] Chen JL, Zheng GS, Xu L, Zhang J, Lu Y, Xue G, Yang YS. Polymer 2001;42:4459.
[14] Wunderlich B. Thermal analysis. New York: Academic Press; 1990. p. 205.
[15] Petrie SEB. J Polym Sci: Part A-2 1972;10:1255.
[16] Wysgoski MG. J Appl Polym Sci 1980;25:1455.
[17] Matsuoka S. Polym Eng Sci 1974;14:162.
[18] Zhou D, Xue G, Li L, Chen J, Wang Z. Eur Phys J E 2003;11:111.
[19] Berens AR, Hodge IM. Macromolecules 1982;15:756.
[20] Spevacek J, Suchoparek M. Macromolecules 1997;30:2178.
[21] Saiani A, Guenet JM. Macromolecules 1999;32:657.
[22] Berghmans M, Thijs S, Cornette M, Berghmans H, Schryver de FC. Macromolecules 1994;27:7669.
[23] Spevacek J, Femandez-Pierda I. Markromol Chem 1987;188:861.
[24] Wang J, Zhao J, Gu Q, Shen D. Macromol Rapid Commun 2001;22:948.
[25] Gu Q, Song R, Shen DY. Polym Bull 2000;44:533.
[26] Hodge IM, Berens AR. Macromolecules 1985;18:1980.
[27] Hens Y, Prud'homme RE, Schultz J. Macromolecules 1998;31:2545.