Polymer 42 (2001) 4459–4462

polymer

www.elsevier.nl/locate/polymer

Polymer Communication

Spectroscopic study of ordered structures of atactic poly(methyl methacrylate) freeze-extracted from poly(ethylene glycol) solution

Jinglu Chen[a], Guishan Zheng[a], Long Xu[a], Jun Zhang, Yun Lu[a], Gi Xue[a,*], Yingsong Yang[b]

[a]*The State Key Laboratory of Functional Polymer Materials for Adsorption and Separation at Nankai, Department of Chemistry, Chemistry Building, Nanjing University, Nanjing 210093, People's Republic of China*

[b]*Petrochemical Institute of East China University of Science & Technology, Shanghai 200540, People's Republic of China*

Received 22 August 2000; received in revised form 10 October 2000; accepted 12 October 2000

Abstract

The conformation of atactic poly(methyl methacrylate) (a-PMMA) freeze-extracted from solvents of various molecular size was investigated by IR and Raman spectroscopy. IR studies showed that self-aggregates and partial helix conformation of polymer chain existed in the annealed a-PMMA sample freeze-extracted from a-PMMA/poly(ethylene glycol) (PEG) solution. Temperature dependence of IR $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ ratio indicated that a-PMMA freeze-extracted from PEG had lower backbone conformational energy than that from dioxane. FT-Raman spectroscopies showed that strong interaction existed between a-PMMA and dioxane, while little solute–solvent interaction existed in the a-PMMA/PEG system. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Atactic poly(methyl methacrylate); Ordered structure; Self-aggregate

---

1. Introduction

The solution and solid state behaviours of syndiotactic poly(methyl methacrylate) (s-PMMA) have been studied extensively by different authors in recent years [1–6]. The degree of stereoregularity and solvent quality play a major role in the formation of ordered chain structures. It has been found that both self-aggregates and stereocomplex of s-PMMA can be formed in some organic solvents [5–10].

The changes in molecular conformation can be followed by infrared spectroscopy [1,3]. The absorption band at 860 cm^{-1} is characteristic for the all *trans* or close to the all *trans* (*TT*) conformation. The *trans–gauche* conformation (*TG*) absorbs at 843 cm^{-1} and is characteristic of the random coil. The intensity ratio of these two signals (*TT*/*TG*) has been used to measure the degree of random coil to helix transformation. The formation of aggregates is manifested by infrared spectra in the range of C=O stretching vibrations by the appearance of a new band at 1741 cm^{-1} owing to interactions between eater groups from the interacting s-sequences [4]. These ordered structures are preserved partly in the solid state, and that is a prerequisite of the formation of crystalline structure [8].

As to atactic poly(methyl methacrylate) (a-PMMA), intramolecular coil to helix transition and self-aggregation was not found by IR measurement either in its solution or in the solid state [1]. Fluorescence anisotropy study of the pyrene labeled a-PMMA showed that no fluorescence anisotropy was found in a-PMMA/toluene solution at any concentration [11]. NMR study also concluded that no association was detected in solutions of a-PMMA in bromobenzene [9]. However, we observed that partially ordered structures could be formed in freeze-extracted a-PMMA sample from solvent of large molecules after annealing. In this paper, the self-aggregation and formation of ordered structures of a-PMMA freeze-extracted from low molecular weight poly(ethylene glycol) (PEG) will be reported by means of infrared spectroscopy and Raman spectroscopy.

2. Experimental

2.1. Materials

a-PMMA was prepared by radical polymerization with dibenzoyl peroxide as initiator. Molecular weight of the a-PMMA sample was characterized by viscosity measurements in toluene at 25°C: $M_{\mathrm{v}} = 7.75 \times 10^5$. The tacticity of the sample was determined in deuterated chloroform by means of 500 MHz proton NMR spectroscopy. The

---

* Corresponding author. Tel.: +86-25-359-2569; fax: +86-25-331-7761.
E-mail address: xuegi@nju.edu.cn (G. Xue).

PII: S0032-3861(00)00749-7

proportions of syndiotactic, heterotactic and isotactic triads were 60.1, 35.3 and 4.6%, respectively. The PEG solvent with an average molar mass of 400 was supplied by Liming Chemical Institute in China.

2.2. Sample Preparation

The freeze-extracted samples were prepared by adding a desired amount of a-PMMA/PEG or a-PMMA/dioxane mixture into a 10 ml Erlenmeyer flask. The mixture was initially heated to 150°C (to a-PMMA/dioxane system, the heating temperature was 95°C) while stirring in a silicon oil bath under nitrogen atmosphere, then held at this temperature for 5 h to ensure that the a-PMMA was completely dissolved in the PEG or dioxane and a homogeneous solution was obtained. The polymer concentration was 5 wt%. The solution was then poured into liquid nitrogen to freeze the binary system in a fraction of a second. The PEG or dioxane solvent was extracted by adding large amount of cold ethanol at a temperature below the melting point of the solvent into the frozen a-PMMA/PEG or a-PMMA/dioxane system. After the initial extraction, the slightly swollen a-PMMA was extracted overnight at room temperature in a large excess of ethanol. This procedure was repeated five times. The powdered a-PMMA was separated by ultracentrifugation and dried in vacuum drying oven for 24 h at room temperature. For the obtained a-PMMA powder, no weight loss was observed in thermogravimetry analysis (Thermal Analyst 2100, TA Instruments), and no solvent absorption band appeared in its IR spectra. These results indicated that no detectable PEG or dioxane solvent existed in the freeze-extracted a-PMMA samples. The freeze-extracted samples were annealed for 30 min at 140°C, which is just above its glass transition temperature.

2.3. Experimental methods

FT-IR spectra were recorded using a Bruker IFS66V FT-IR spectrometer. The powdered samples were dispersed in KBr pallets. In situ variable temperature IR measurements were made with a heating cell. In the analysis of the spectra, peak heights were used as the relative band intensity. Cooling the 5 wt% a-PMMA/PEG solution obtains an opaque gel, while 5 wt% a-PMMA/dioxane system keeps a transparent solution. FT-Raman spectra of 5% a-PMMA/PEG gel and a-PMMA/dioxane solution were recorded with 1.064 nm excitation, using a Bruker RFS100 FT-Raman spectrometer.

3. Results and discussion

Fig. 1 shows the IR spectra in the range of 900–800 cm^{-1} and carbonyl stretching vibration bands for freeze-extracted a-PMMA samples before and after annealing. No significant change was found for the annealed a-PMMA sample freeze-extracted from dioxane, as shown in Fig. 1A and B. However, for the annealed a-PMMA sample freeze-extracted from PEG, two important changes were found in Fig. 1C and D. First, in the range of carbonyl stretching vibrations, the carbonyl band has splitted into two bands and a component at higher wavenumber (1741 cm^{-1}) appears. The band at higher wave numbers, which appears only in the spectra of dilute solution in toluene or cast film of syndiotactic PMMA [1,5], evidently corresponds to the carbonyl stretching vibrations in aggregated units owing to interactions between ester groups from the interacting s-sequences [4,10]. We have separated the two bands under the assumption that they are Lorentzian and that the integral absorbance coefficients are the same for both bands. The fraction of the aggregated a-PMMA is 61.5%, indicating that considerable amount of a-PMMA segments are in aggregated state. Second, a shoulder band appears at 860 cm^{-1} after annealing, and it is characteristic for the all trans or close to the all *trans* (*TT*) conformation [11]. Theoretical calculations designate this slightly deformed *TT* conformation as the energetically most stable on which the helix conformation of the polymer chain is based [4]. The *trans–gauche* conformation (*TG*) absorbs at 843 cm^{-1} and is characteristic of the random coil. From Fig. 1D it is seen that, for the annealed a-PMMA sample freeze-extracted from PEG, self-aggregates of a-PMMA had formed and partial helix conformation of the polymer chain existed in the solid state.

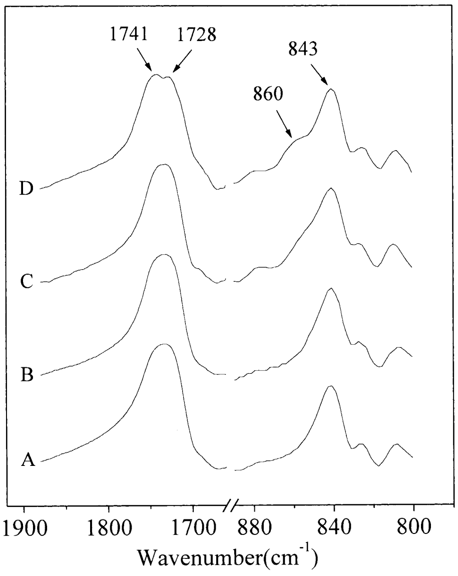

Fig. 1. FT-IR spectra of a-PMMA samples: (A) freeze-extracted from dioxane; (B) sample A after annealing at 140°C for 30 min; (C) freeze-extracted from PEG; D, sample C after annealing at 140°C for 30 min.

Fig. 2 shows expanded IR spectra in 1300–1000 cm^{-1} range of a-PMMA freeze-extracted from PEG before and after annealing. Four absorption bands can be observed which are assigned to the ν_a (C–C–O) vibration coupled to the ν(C–O) vibration. These bands can be used to study the conformation changes of a-PMMA since it is known to be conformation sensitive [12]. Absorption peaks at 1270 and 1240 cm^{-1} have been used to calculate the van't Hoff

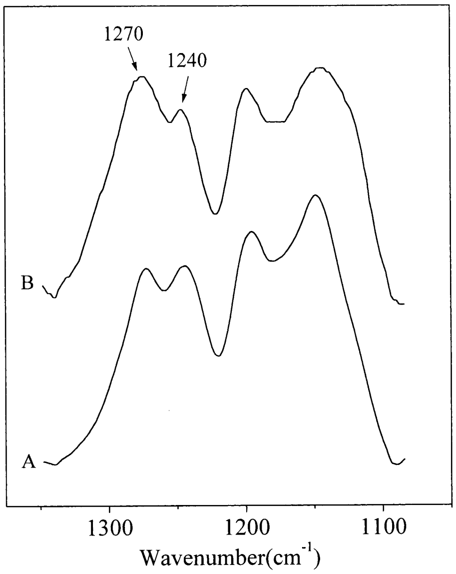

Fig. 2. Expanded FT-IR spectra in 1300 − 1000 cm^{-1} range of a-PMMA samples: (A) Freeze-extracted from PEG, and (B) sample A after annealing at 140°C for 30 min.

conformational energies [13], and the IR I_{1240} cm^{-1}/I_{1270} cm^{-1} ratio is used to give the ratio of the backbone conformational energy relative to the overall energy of the chain segment [14]. A high ratio indicates that the backbone conformation imposes the chain conformation while a low ratio is related to a local equilibrium between backbone and side-chain conformations. It can be found in Fig. 2 that the annealed a-PMMA freeze-extracted from PEG has lower IR $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ ratio than the unannealed sample, indicating that strong interaction exists between carbonyl groups which increases the conformational energy of the side chain for the annealed a-PMMA sample freeze-extracted from PEG. This phenomenon was also found in Spevacek's study that the s-PMMA film in ordered structures has lower IR $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ ratio than that in the randomly coiled s-PMMA [1].

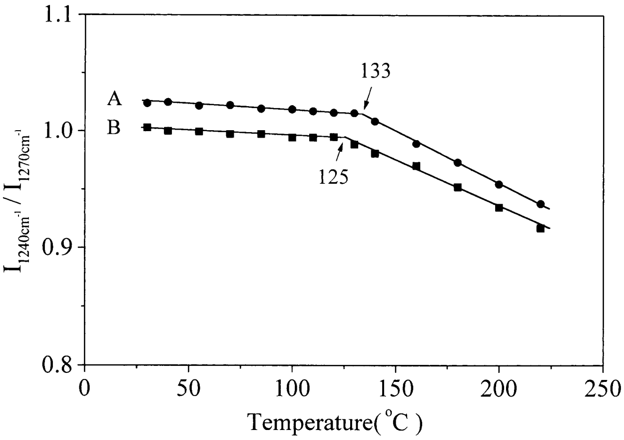

Fig. 3. Temperature dependence of IR $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ ratio of a-PMMA samples: (A) freeze-extracted from dioxane; and (B) freeze-extracted from PEG.

Fig. 3 shows the temperature dependence of IR intensity ratio $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ of freeze-extracted a-PMMA samples. An obvious transition temperature is seen from two curves, which can be ascribed to the glass transition of polymer segments [14]. The decrease in intensity ratio $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ can be related to a decrease of the backbone conformational energy relative to the chain segment conformational energy. Above the glass transition temperature, high energy conformations (*TG*) of the backbone are known to be more favored and may originate from a weaker control of the segment conformation by the backbone, leading to a decrease of the IR intensity ratio. Differences are observed in Fig. 3 between the freeze-extracted a-PMMA samples from dioxane (curve A) and PEG (curve B) solvent. The IR intensity ratio in curve B is lower than that of curve A, and the turning point is seen at 133°C in curve A and at 125°C in curve B. There is 8°C difference between the two turning points of these curves. The differences in IR intensity ratio between curve A and curve B can be interpreted that the a-PMMA freeze-extracted from PEG has lower backbone conformational energy relative to the overall energy of the chain segment than that from dioxane. This means that the interaction between carbonyl groups, which increases the conformational energy of the side chain, is stronger in the a-PMMA freeze-extracted from PEG than that from dioxane. For the a-PMMA freeze-extracted from PEG, self-aggregates of some segments can be formed after annealing as its lower backbone conformational energy comparing with the sample freeze-extracted from dioxane. The formation of ordered structure in a-PMMA reinforces the side-group interactions, i.e. increases the side-chain conformational energy, and results in the lower IR intensity ratio $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ as shown in Fig. 2B.

The lower glass transition temperature of a-PMMA freeze-extracted from PEG may probably originates from the less entanglements existed in the freeze-extracted a-PMMA from PEG than that freeze-extracted from dioxane [15,16]. Fig. 4 and Fig. 5 show the FT-Raman spectra of

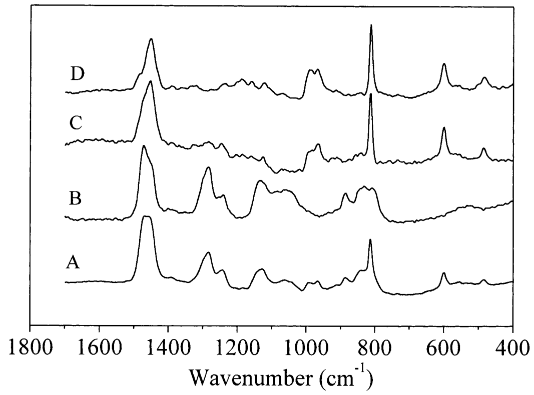

Fig. 4. FT-Raman spectra recorded from: (A) a-PMMA/PEG gel; (B) PEG; (C) subtraction of A − B, and (D) control a-PMMA.

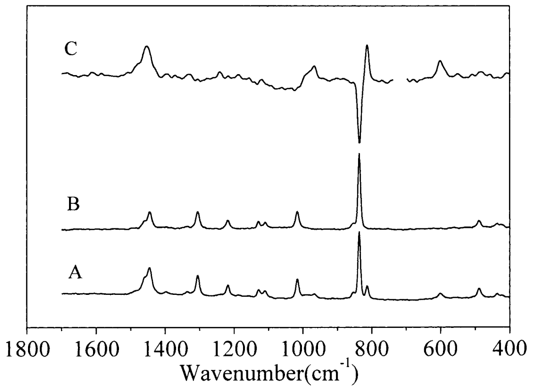

Fig. 5. FT-Raman spectra recorded from: (A) a-PMMA/dioxane solution; (B) dioxane; and (C) subtraction of A − B.

a-PMMA samples dissolved in PEG and dioxane, respectively. Fig. 4A, B and D are the Raman spectra of 5 wt% a-PMMA/PEG gel, pure PEG solvent, and control a-PMMA, respectively. Fig. 4C is the subtraction spectrum (4A − 4B), which is similar to the spectrum of control a-PMMA. Fig. 5A and B are the Raman spectra recorded from 5 wt% a-PMMA/dioxane solution and pure dioxane, respectively. The spectrum of Fig. 5C is the subtraction spectrum (Fig. 5A − B). The difference spectrum of Fig. 5C is quite different from that of control a-PMMA (Fig. 4D), indicating the existence of strong interaction between a-PMMA and dioxane which caused some Raman lines of a-PMMA to shift from their original positions, while in the a-PMMA/PEG gel, little solvent–solute interaction existed. The interactions between dioxane and a-PMMA reduce the intramolecular interactions between side groups, therefore in the semidilute a-PMMA/dioxane solution, the intermolecular interactions in PMMA were strong and the polymer chains are in the serious entangled state. While in the a-PMMA/PEG system, PMMA interchain entanglements are partially replaced by PMMA/PEG interpenetration as the relatively long chain in PEG oligomer compared to the normal small molecule solvents. The movement of PMMA chain in the environment of PEG molecules may be represented by the reptation model proposed by de Gennes [17,18]. For a PMMA molecule, PEG imposes only a weak constraint and allows the long chain to move in a rapidly renewed tube, while other PMMA chains which entangled with the chain of interest can only translate slowly due to the restriction of PEG chains. This resulted in the less entanglement of PMMA chains freeze-extracted from PEG solvent than that of from dioxane solvent.

4. Conclusions

The doublets of carbonyl stretching band near 1741 cm^{-1} corresponding to the self-aggregates of a-PMMA in its IR spectrum was found in the annealed a-PMMA sample freeze-extracted from a-PMMA/PEG solution. A shoulder band in 860 cm^{-1} in its IR spectrum, which is characteristic for the all *trans* or close to the all *trans* (*TT*) conformations, indicated that partial helix conformation of polymer chain existed in the solid state. Temperature dependence of IR $I_{1240\ \mathrm{cm}^{-1}}/I_{1270\ \mathrm{cm}^{-1}}$ ratio showed that a-PMMA freeze-extracted from PEG had lower backbone conformational energy than that from dioxane, and self-aggregates can be formed after annealing. FT-Raman spectroscopies showed that strong interaction existed between a-PMMA and dioxane, while little solute–solvent interaction existed in the a-PMMA/PEG system.

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China.

References

[1] Spevacek J, Schneider B, Dybal J, Stokr J, Baldrian J. J Polym Sci , Polym Phys Ed 1984;22:617.
[2] Konnecke K, Rebage G. Colloid Polym Sci 1981;259:1062.
[3] Dybal J, Stokr J, Schneider B. Polymer 1983;24:971.
[4] Spevace J, Schneider B. Adv Colloid Interface Sci 1987;27:81.
[5] Dybal J, Spevacek J. Makromol Chem 1988;189:2099.
[6] Saiani A, Spevacek J, Guenet JM. Macromolecules 1998;31:703.
[7] Yamaguchi S, Hayashi H, Hamada F, Nakajima A. Macromolecules 1984;17:2131.
[8] Spevacek J, Schneider B, Baldrian J, Dybal J, Stokr J. Polym Bull 1983;9:495.
[9] Spevacek J, Suchoparek M. Macromolecules 1997;30:2178.
[10] Spevacek J. Makromol Chem Macromol Symp 1990;39:71.
[11] Berghmans M, Thijs S, Cornette M, Berghmans H, De Schryver FC. Macromolecules 1994;27:7669.
[12] Willis HA, Zichy VJ, Hendra PJ. Polymer 1969;10:737.
[13] O'Reilly JM, Mosher RA. Macromolecules 1981;14:602.
[14] Grohens Y, Prud'homme RE, Schultz J. Macromolecules 1998;31:2545.
[15] Dai Q, Lu Y, Xue G, Liao YT. Polym Bull 1995;35:209.
[16] Huang D, Yang Y, Zhang G, Li B. Macromolecules 1999;32:6675.
[17] de Gennes PG. J Chem Phys 1971;55:572.
[18] Doi M, Graessley WW, Helfand E, Pearson DS. Macromolecules 1987;20:1900.