

Living polymerization of α -methylstyrene in tetrahydrofuran followed by dynamic light scattering near its polymerization temperature

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(Received 24 September 1998; accepted 2 April 1999)

We followed the polymerization reaction of living poly- α -methylstyrene in a solution of tetrahydrofuran as a function of temperature, near its ceiling temperature, using dynamic light scattering. We obtained three different relaxation times revealing three kinds of macromolecular species in the solution. One of the relaxation times corresponded to the formation of living polymer chains. In this particular case, we found that the average relaxation time increased as temperature was lowered due to polymer growth. Nevertheless, it did not follow the same track along a cooling–heating cycle. These results are consistent with an incomplete depolymerization reaction. For the other two species, we propose that they were the result of ionic aggregation. © 1999 American Institute of Physics. [S0021-9606(99)52722-0]

In general, there is a temperature below which vinyl monomers can be polymerized, if the appropriate method of polymerization is used for a given monomer.^{1,2} In most of the polymerization reactions, a negative free energy is reached when the system is cooled to the so called “ceiling temperature.” There is no polymer formation above the ceiling temperature.^{1–3} For polymers initiated by an ionic mechanism, equilibrium between monomer and their polymeric chains can be reached at the ceiling temperature, in the absence of polymer deactivating contaminants.³ These are known as “living polymers,” due to their capability of being polymerized by lowering their temperature or by adding more monomer, and their capacity for being depolymerized when temperature is raised again.⁴

Ceiling temperatures for most living polymerization reactions are often well above 373 K. Thus, the equilibrium position of the propagation-depropagation reaction is by far shifted towards the polymer formation at room temperature, i.e., a complete incorporation of monomers into the polymer chains.^{2,5} However, there are some monomers for which the ceiling temperatures are relatively low. An example is α -methylstyrene (α -MS), which has a ceiling temperature of about 334 K.^{2,5} If a solvent is added, the ceiling temperature can be lowered even more.^{2,6,7} α -MS has been studied near the polymerization line in solution, with tetrahydrofuran and methylcyclohexane.^{7–13} In the case of the tetrahydrofuran solution, small-angle neutron scattering (SANS) measurements have been reported.¹⁰ These results were discussed within the framework of the mean field theory and of the n -vector theory of magnetism, considering the onset of the polymerization reaction as a second order phase transition.

Light scattering techniques have been extensively applied to the study of polymer solutions.^{14,15} However, most

of the work has been devoted to the study of “dead” polymers; polymers where the ends are not active and therefore can not longer grow or depolymerize. Fetters *et al.*^{16,17} studied living polystyrene in benzene using sec-butyllithium as initiator, at room temperature. They report the formation of polymeric dimers and of polymerlike micelles. In their experiments, the equilibrium was shifted towards polymer formation as a consequence of the high ceiling temperature of styrene of about 250 °C; all monomers were incorporated into the polymer chains and depolymerization was unlikely.

As far as we know, no dynamic light scattering (DLS) studies have been reported following the polymerization and the depolymerization reactions of a living polymer in solution as a function of temperature, near its ceiling temperature. Here, we present an experiment which follows the polymerization of a solution of living poly- α -methylstyrene (P- α -MS) in tetrahydrofuran (THF), using DLS near its ceiling temperature, and using sodium-naphthalide complex as the initiator.^{3,7}

α -MS (99%) and THF (99.9% anhydrous) were further purified in a high-vacuum line, using standard purification and handling techniques.^{18,19} Sodium (99.95%) and naphthalene (>99%) were used as purchased. The initiator, sodium-naphthalide complex, was formed by reacting sodium with naphthalene in tetrahydrofuran, and was used fresh at a concentration of 6.54×10^{-3} mol/l. The monomer and the initiator solution were filtered using separately gas-tight syringes with a 0.2 μ m Millipore filter attached. The sample was prepared in 12 mm NMR tubes by adding a known amount of α -MS monomer to a known amount of initiator solution. The cell was closed with a septum. A low vacuum was quickly made throughout the septum to help to seal off the cell permanently. The sample was sealed off without any previous freezing below its ceiling temperature and with a negligible loss of sample. To prevent contamination, all the

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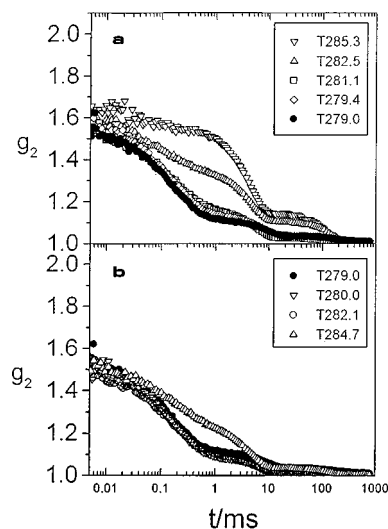


FIG. 1. Intensity correlation functions, g_2 , of the scattered light against the delay time for the living poly- α -MS, at different temperatures along a cooling-heating cycle. (a) On cooling; (b) on heating.

sample preparation and low vacuum operations were performed inside an inert argon atmosphere self-cleaning glovebox. All materials used inside the glovebox were washed with the initiator solution, to destroy any remaining impurities that could deactivate the polymer, and then washed with clean THF. This procedure gives about 5% of deactivation in one of the ends of the total chains.²⁰ The monomer molar fraction was $X_m = 0.174$. We estimated the ceiling temperature to be close to 282 K using the ceiling temperature line given by Greer.⁷ Our sample had an initiator to monomer molar ratio of 3.43×10^{-3} . It is important to note that our DLS experiments were performed with a sample not previously polymerized.

Light scattering experiments were performed in a conventional setup for homodyne detection. Laser light was produced by a He-Ne laser. A 25 cm focusing lens was used to focus a 14 mW beam in the center of the cell at 30° from the detection direction ($q = 7.35 \times 10^{-4} \text{ \AA}^{-1}$). The cell was immersed in a temperature controlled circular water bath. Temperature was kept constant within 0.1 K. The coherence area was optimized for dynamic light scattering. Scattered light was detected with a photomultiplier and electrical signals were preamplified and shaped with a preamplifier/discriminator. Counts per second and correlation functions were obtained by a multiple-tau correlator (ALV 5000). Light-scattering measurements were obtained after at least 180 min of thermal stabilization of the sample to assure that it had relaxed.²¹ Our exposure times were not large, to prevent degradation of the samples. Typical measurement times were 5–7 min. In similar samples, we were unable to detect polymer degradation within these exposure times.

We followed the polymerization reaction as a function of temperature. Figure 1 shows the intensity correlation functions of the scattered light. The correlation functions were obtained at different temperatures along a cooling-heating cycle of the sample. In Fig. 1, three different relaxation times are seen revealing three kinds of macromolecular species. In

Fig. 1(a), the upper curve was obtained at a temperature little above T_c . Here, two different relaxation times are observed ($\tau \sim 10$ ms and $\tau \sim 100$ ms) corresponding to two large species. The other four curves were obtained little above and below T_c . As the temperature was lowered, the growing of a new molecular species was clear at lower relaxation times ($\tau \sim 0.2$ ms). As this new species grew, the largest species at $\tau \sim 100$ ms appeared to be destroyed. The temperature at which the new species appeared agrees with the expected polymerization temperature for this sample concentration and therefore suggests that the growing species are the living chains of Poly- α -MS, which grow at the expense of the largest species. Above T_c , we observed that the index of refraction of the monomer solution was quite dependent on light intensity (starting around 12–15 mW), similar to the case of nematic liquid crystals. This observation is consistent with the formation of a long-linear association of initiated dimers, like long threads (the largest aggregates at $\tau \sim 100$ ms), acting as a source for the growth of a living polymer. At T_c , this association breaks down, releasing the associated dimers to start the polymerization.

Fetters *et al.*¹⁶ have reported dimeric and micellarlike association of living polystyrene in benzene initiated by lithium alkyls, with chains having only one living end. More recently, Stellbrink *et al.*¹⁷ have used SANS to elucidate the structure of aggregates of styryllithium in the early stages during anionic polymerization in benzene. They found the presence of dimer and trimer aggregates. In addition they also found the formation of large fractal-like aggregates with sizes above 1000 Å. These results were unexpected, since the dimer had been assumed to be the maximum allowable aggregate, because of living styryllithium has only one living end.

In the case of living Poly- α -MS, since the dissociation constant for contact-ion pairs into free ions is very small,^{3,22} the chains have two living ends with ion-pairs in contact. Thus, a long associated chain aggregate could be possible through dipole interaction, since THF is only a moderately polar solvent ($\epsilon = 7.39$ at 298 K).³ On heating, Fig. 1(b), we observed the depolymerization of the living polymer chains, though some of them still remained above T_c . We also observed that the largest associated species ($\tau \sim 100$ ms) reappeared to some extent. The species at intermediate relaxation times ($\tau \sim 10$ ms) are quite stable and could be similar to those reported by Fetters *et al.*,¹⁶ corresponding to polymeric micellar structures, whose size does not change largely on cooling and on heating. They presented some growth as we cool down the samples (relaxation times $\tau \sim 12$ ms at 285.59 K and $\tau \sim 28$ ms at 279 K). To prevent sample degradation through light exposure,²³ we did not study the dependence of the relaxation modes with respect the scattering angle. However, it has been reported that with living polystyryllithium the relaxation modes are diffusive,¹⁶ i.e., they depend linearly on the square of the scattering vector.

In Fig. 2, we present average relaxation times obtained with the Williams–Watts procedure for stretched exponentials,¹⁵ along a cooling-heating cycle for the assumed living polymer chains ($\tau \sim 0.2$ ms). As expected, we found that the average relaxation time increased as tempera-

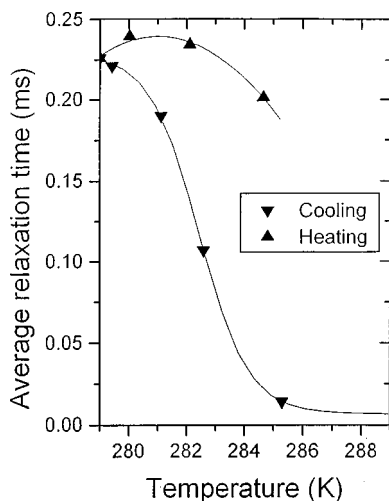


FIG. 2. Average relaxation times for the assumed living chains vs temperature, along a cooling–heating cycle. (Lines are guides to the eye).

ture was lowered, due to polymer growth. The increase in these relaxation times, due to the growth of the linear living polymers, was about one order of magnitude, while that corresponding to the micellar structures ($\tau \sim 10$ ms, not shown) increased by a factor of nearly 2. The average relaxation time did not follow the same track on the heating run as on the cooling run. That shows evidence of the existence of larger species in the solution, on the heating run above T_c . These results are consistent with an incomplete depolymerization reaction. Similar results were obtained with shear viscosity measurements in this kind of system.²¹ An estimated hydrodynamic radius, R_h , at the lowest temperature reached in our experiment was obtained through the Stokes–Einstein equation using estimated viscosity values.²¹ Our R_h values are of the order of 2–3 nm. The resolution is limited by the uncertainty of the viscosity. Our R_h is close to the 3.66 nm obtained by Fetters *et al.*¹⁶ for the dimeric form of living polystyrene in benzene. Their average molecular weight for complete conversion of the monomer into polymer is of the same order as in our case (1.75×10^4), considering that here we used a more polar solvent.

We report the first DLS study of a living polymer solution near its ceiling temperature; living P- α -MS in THF. We found formation of large macromolecular species that can be

explained by an ionic aggregation between the living ends. Our results are consistent with those reported for living polystyrene in benzene,^{16,17} in the sense that ionic living polymerization reactions are more complex than previously thought.

We thank to S.C. Greer for allowing us to use her laboratory facilities for the preparation of the living polymer samples. We acknowledge support from CONACYT and DGAPA-UNAM under Grants Nos. 2072P-E9507 and IN100595, respectively. J. R.-G. also acknowledges support of the Chemistry Division of the National Science Foundation.

¹H. Sawada, *Thermodynamics of Polymerization* (Dekker, New York, 1976).

²G. Odian, *Principles of Polymerization*, 3rd ed. (Wiley, New York, 1991).

³M. Szwarc, *Carbanion, Living Polymers, and Electron Transfer Process* (Wiley, New York, 1968).

⁴M. Szwarc, *Nature (London)* **178**, 1168 (1956).

⁵*Polymer Handbook*, 3rd ed., edited by J. Brandup and H. E. Immergut (Wiley, New York, 1989).

⁶F. S. Dainton and K. J. Ivin, *Nature (London)* **162**, 705 (1948).

⁷S. C. Greer, *Adv. Chem. Phys.* **XCIV**, 261 (1996).

⁸K. M. Zheng and S. C. Greer, *Macromolecules* **25**, 6128 (1992).

⁹K. M. Zheng, S. C. Greer, L. R. Corrales, and J. Ruiz-Garcia, *J. Chem. Phys.* **98**, 9873 (1993).

¹⁰A. P. Andrews, K. P. Andrews, S. C. Greer, F. Boue, and P. Pfeuty, *Macromolecules* **27**, 3902 (1994).

¹¹S. Sarkar Das, A. Poplis Andrews, and S. C. Greer, *J. Chem. Phys.* **102**, 2951 (1995).

¹²J. Zhuang, A. Poplis Andrews, and S. C. Greer, *J. Chem. Phys.* **107**, 4705 (1997).

¹³S. C. Greer, *J. Phys. Chem.* **102**, 5413 (1998).

¹⁴W. Brown, *Light Scattering* (Clarendon, Oxford, 1996).

¹⁵*Dynamic Light Scattering*, edited by W. Brown (Clarendon, Oxford, 1993).

¹⁶L. J. Fetters, N. P. Balsara, J. S. Huang, H. S. Jeon, K. Almdal, M. Y. Lin, *Macromolecules* **28**, 4996 (1995).

¹⁷J. Stellbrink, L. Willner, O. Jucknischke, D. Richter, P. Lindner, L. J. Fetters, and J. S. Huang, *Macromolecules* **31**, 4189 (1998).

¹⁸L. J. Fetters, *J. Res. Natl. Bur. Stand.* **70A**, 421 (1996).

¹⁹J. Ruiz-Garcia, Ph.D. dissertation, The University of Maryland at College Park, 1989.

²⁰J. Zhuang, S. Sarkar Das, M. D. Nowakowski, and S. C. Greer, *Physica A* **244**, 522 (1997).

²¹J. Ruiz-Garcia and S. C. Greer, *J. Mol. Liq.* **71**, 209 (1997).

²²J. Comyn, F. S. Dayton, G. A. Harpell, K. M. Hui, and K. J. Ivin, *Polym. Lett.* **5**, 965 (1967).

²³K. P. Andrews, Ph.D. dissertation, The University of Maryland at College Park, 1994.