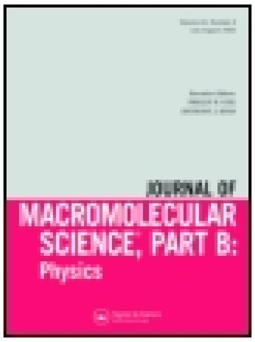

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On the Cryogenic "Degradation" of Polystyrene in Dilute Solution

SONG WANG, XIAOHU YAN, JIANFU DING, MINGZHU LIU, and
RONGSHI CHENG*
Department of Chemistry
Nanjing University
Nanjing 210093, P.R. China

CHI WU
Department of Chemistry
The Chinese University of Hong Kong
Shatin, N.T., Hong Kong

RENYUAN QIAN
Institute of Chemistry
Academia Sinica
Beijing 100080, P.R. China

ABSTRACT

The effect of cryogenic treatment on dilute polystyrene solutions of different thermal history was studied by viscometry, size-exclusion chromatography, and static laser light-scattering measurements. The lowering of apparent molar mass during freezing of the solvent has its origin in a more compact conformation of the polymer chain resulting from the formation of intrachain segmental cohesion. Prior hypotheses about cryogenic degradation or chain scission in the polymer solution are incorrect.

Key Words. Cryogenic degradation; Intrachain cohesional entanglement.

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*To whom correspondence should be addressed.

Since Berlin et al. [1] introduced the cyclic freezing and thawing process to study the effect of cryogenic treatment on dilute polymer solutions, later investigators [2–9] have all claimed that long-chain macromolecules undergo degradation during freezing of the solvent. This conclusion was reached from measured viscometric [2–4] and size-exclusion chromatographic (SEC) [5–9] data. The phenomena of decreasing solution viscosity and increasing retention volume of SEC were regarded as the result of degradation of the polymer chain, that is, lowering of the molar mass of the polymer.

The formation of cryogenic hydrogel of water-soluble polymers by freezing their aqueous solutions is a phenomenon known for many years. Undoubtedly the gel formation is the result of intermolecular physical crosslinking. In a study on the concentration dependence of gel formation of aqueous polyvinyl alcohol solutions, we found that no visible hydrogel was formed for concentrations below the gelation threshold C_{gel} situated in the vicinity of 10^{-5} g/mL. This characteristic concentration is near the critical concentration for coil shrinking C_S and is much lower than the overlap concentration C^* [10]. Recently, we studied the effect of cryogenic treatment on an extremely dilute aqueous solution of polyvinyl alcohol by measuring its solution viscosity. It was found that on applying cyclic freeze–thaw treatment, intrachain physical crosslinking or intrachain cohesional entanglement occurred [11], analogous to intermolecular hydrogel formation. It is believed that in the case of polyvinyl alcohol the crosslinks are hydrogen bonds between pendant hydroxyl groups. These facts led us to consider that cryogenic degradation may be problematic as the change of the polymer chain conformation, such as collapse of a coil to a globule, may also lead to the same apparent changes of solution viscosity and the size-exclusion chromatographic profile.

It is not difficult to distinguish whether polymer chains are undergoing degradation or forming stable globules due to intrachain cohesional entanglement during cryogenic treatment. Since degradation is nonreversible and globule formation is reversible, we only need to examine whether the decrease of viscosity or the increase of the SEC elution volume after cryogenic treatment can be recovered or not by heating the freeze-treated solution or by other means to enhance the globule-to-coil transition.

It is known that both isotactic and atactic polystyrene in some organic solvents such as carbon disulfide undergo gelation upon cryogenic treatment [12,13]. To clarify the question whether cryogenic degradation actually occurred or not for polystyrene in non-gel-forming solvents, some experiments were carried out to investigate the effect of cryogenic treatment.

First we chose tetrahydrofuran as a solvent for a polystyrene sample and as the eluent for its SEC. A number of solutions in the concentration range from 1×10^{-4} to 1×10^{-6} g/mL, dilute enough to avoid interchain interactions, were characterized by SEC. The solution in a test tube was subjected to cryogenic treatment by immersion in liquid nitrogen for a few minutes, and then the frozen solution was thawed at ambient temperature and characterized by SEC again. No detectable difference of SEC chromatograms was observed for the solution which had been subjected to cryogenic treatment as compared to the original SEC profile. After repeating the freeze–thaw cycles 100 times, the SEC profile obtained was still identical to the original one. These facts indicate that no chain degradation takes place for polystyrene in tetrahydrofuran during cryogenic treatment.

Benzene was also used as a solvent for a polystyrene solution at a concentration of 1×10^{-3} g/mL in a stoppered test tube. Following cryogenic treatment of repeated freezing-thawing cycles 100 times, the viscosity and SEC profile of the benzene solution were measured at once. The relative viscosity of the solution changed from 1.543 to 1.515 after treatment, a remarkable 5.2% decrease in specific viscosity that is similar to the decrease reported in the literature. However, when the cryogenic-treated benzene solution was diluted to 1×10^{-4} g/mL with tetrahydrofuran and then injected into SEC equipment with tetrahydrofuran as eluent, the chromatogram obtained was identical to that of the original sample. At this stage, some qualitative conclusions were reached: (1) The decrease in solution viscosity of benzene solution after cryogenic treatment is due to the change of macromolecular conformation from an expanded coil to a state of more compact conformation, probably involving some intramolecular segmental cohesion between neighbouring segments in space as intramolecular cohesional entanglements. (2) These cohesional entanglements, once formed by cryogenic treatment, are stable in benzene at ambient temperature, and the relaxation from compact conformation to expanded coil conformation is hindered. (3) The stability of these intersegmental cohesion depends upon the solvent-segment interactions. In tetrahydrofuran the intersegmental cohesion seems to be quickly disentangled.

In order to verify the conclusions cited above, we repeated the experiment of cryogenic treatment of benzene solution in a number of sealed glass tubes, but using benzene as SEC eluent instead of tetrahydrofuran. The SEC profiles were determined both for the original solution and for the solutions after 100 and 200 cycles of liquid nitrogen freezing and ambient temperature thawing. Then the cryogenic-treated solutions in the sealed glass tubes were heated in boiling water for half an hour with occasional hand shaking, and size-exclusion chromatography was run again. The chromatograms obtained for these solutions are shown in Figs. 1 and 2.

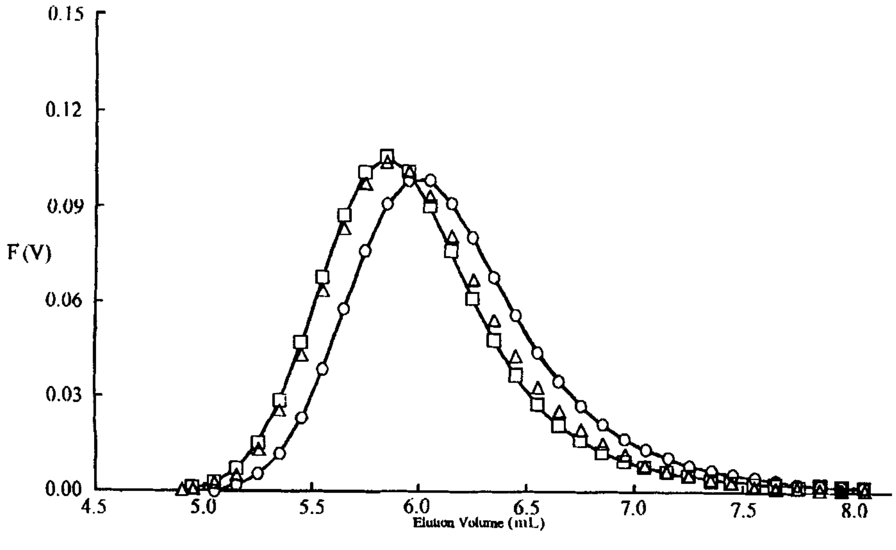

FIG. 1. SEC profiles of polystyrene in benzene: □, original solution; ○, after 100 times of freeze-thaw cycling; △, after reheating the frozen solution.

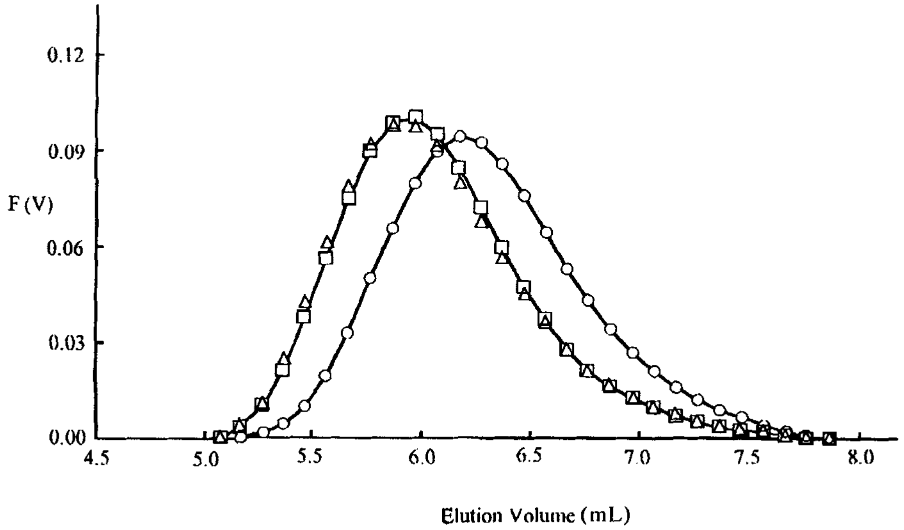

FIG. 2. SEC profiles of polystyrene in benzene: □, original solution; ○, after 200 times of freeze–thaw cycling; △, after reheating the frozen solution.

These two figures clearly show that the SEC profiles of the cryogenic-treated solution moves toward larger elution volume, indicating the hydrodynamic volume of the polymer chains actually decreased during freezing. But after heating the freeze-treated solution to 100°C for half an hour, the SEC profile and hydrodynamic volume of macromolecules reverted to its original state. The reduced hydrodynamic volume of the polymer coil upon solvent-freezing results in an apparent decrease of its molar mass as calculated according to the SEC calibration curve for expanded linear polymer coils. The variation of the relative apparent molar mass for the freeze-treated polystyrene with the number of freezing-thawing cycles is shown in Fig. 3; it is consistent with the results obtained by earlier investigators [2–9]. However, there is no difference between the calculated molar mass for the reheated sample solutions and that of original sample, as also shown in Fig. 3. Now we are sure that there is definitely no chain degradation during freeze–thaw cycling. The compact conformation produced in freezing apparently persisted in solution at room temperatures, as shown by the changed SEC profile. As the conformational changes of a flexible polymer chain should be reversible with rather short relaxation times, the relaxation of the compact conformation produced in freezing must have been locked by the formation of intrachain cohesional entanglements of the individual chains, until the temperature of the solution was raised to 100°C so as to disentangle the intersegmental cohesion. This is similar to the situation in the sub-T_g annealing of a polymer glass rapidly quenched from a temperature higher than T_g [14]. The experimental results also show the morphology of isolated chains are sensitive to the intersegmental cohesion present, although the number of cohesional entanglement points along the chain may be rather small.

The experimental data of solution viscosity and SEC reflect the hydrodynamic volume of macromolecules in solution and relate to the molar mass by empirical

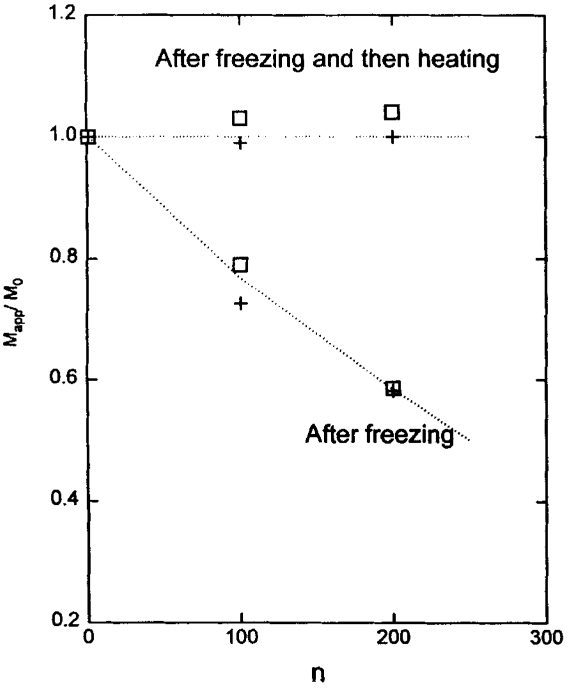

FIG. 3. Variation of apparent molar masses of polystyrene in solutions of different thermal history; n = number of freeze-thaw cycles. □, ratio of weight average molar masses; +, ratio of number-average molar masses.

equations or to the theoretical relationship with certain assumptions. Since these are not absolute methods for polymer molar mass determination, we studied further the effect of cryogenic treatment of polystyrene solution by static laser light scattering for direct determination of the molar mass. A high molar mass polystyrene sample with nominal value of $M_p = 1.44 \cdot 10^7$ from Polymer Laboratories was used to prepare an extremely dilute solution in toluene with $C = 5.8 \cdot 10^{-5}$ g/mL, and the solution was subjected to cyclic liquid nitrogen freezing and subsequent 30°C thawing treatments for 61 times. The angular dependence of the excess scattered light intensities $R(\theta)$ and the specific refractive index increments dn/dC of the original solution and of the solution after the freeze-thaw cycling were measured. Overlooking any possible change of dn/dC—that is, assuming dn/dC of the solution after freeze-thaw is the same as that of the original solution—the plots of the light-scattering function $KC/R(\theta)$ versus q^2 for both solutions are shown in Fig. 4, where $K = 4\pi^2 n^2 (dn/dC)^2/N_A \lambda_0^4$, and $q = (4\pi n/\lambda_0)\sin(\theta/2)$, with N_A, n, and λ_0 being Avogadro's number, solvent refractive index, and the wavelength of the incident light, respectively. In Fig. 4 the data points for the solution after freeze-thaw cycling lies above those of the original solution. By linear regression of the data points of Fig. 4, the reciprocal of the intercept gives the weight average molar mass of the sample in the solution after freeze-thaw cycling as $M_w = 1.27 \cdot 10^7$, which is 15% lower than that of the sample in the original solution, $M_w = 1.49 \cdot 10^7$. However,

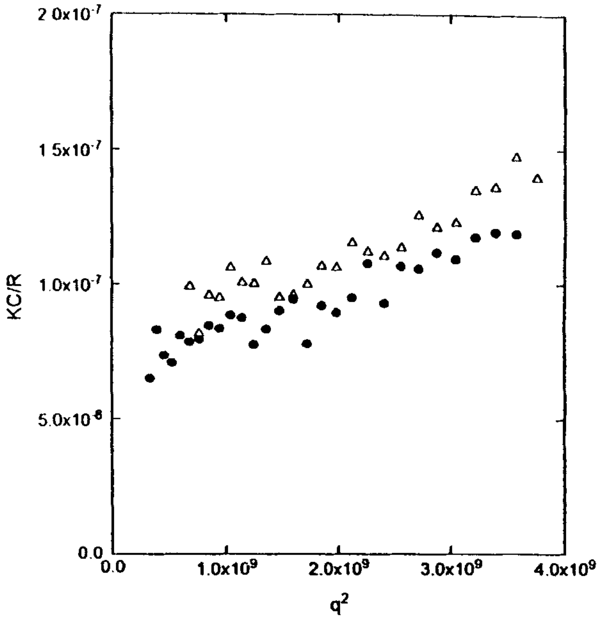

FIG. 4. SLS data for both original polystyrene-toluene solution (●) and after 61 freeze-thaw cycles (△) assuming the same *dn/dC* value (0.114) with the solution concentration of 5.8 · 10^{-5} g/mL.

the measured specific refractive index increments *dc/dC* of the original solution and the solution after freeze-thaw cycling were 0.114 and 0.105, respectively. Taking account of this difference, the resulting $KC/R(\theta)$ versus q^2 plots of the solutions are shown in Fig. 5, in which no distinct difference can be seen for the plots of the solution after freeze-thaw cycling and those of the original solution. That is to say, the weight average molar mass of the sample was not changed after repeated cryogenic treatments. Therefore we may conclude that the hypothesis about cryogenic degradation or chain scission in polymer solution is incorrect. The decrease of *dn/dC* value of the solution after freeze-thaw cycling may have its origin in partial ordering of the solvated solvents associated with the polymer chain in the course of the conformational changes during cryogenic treatments. This subject will be discussed quantitatively in a subsequent paper.

EXPERIMENTAL

Materials

An atactic polystyrene sample of high molar mass with narrow molar mass distribution ($M_w = 1.69 \cdot 10^6$, $M_w/M_n = 1.09$), prepared at Nanjing University, was used for viscometry and SEC studies. An extremely high molar mass polystyrene sample with nominal value M_p (SEC peak) $= 1.44 \cdot 10^7$, $M_w/M_n = 1.21$, from Polymer Laboratories was used for laser light-scattering study. Commercial AR tetrahydrofuran was dried for 2 days and distilled at 66° ~ 68°C. Benzene was

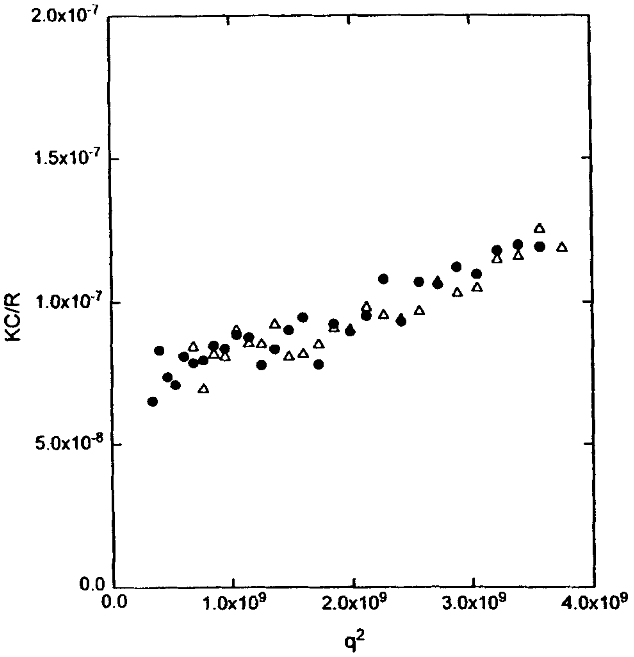

FIG. 5. SLS data of the solutions assuming different *dn/dC* values: ●, original solution, *dn/dC* = 0.114; △, the solution after freeze–thaw cycling, *dn/dC* = 0.105.

purified by the standard method [15], and the distilled fraction was collected between 80° and 82°C. Analytical grade toluene from Riedel-deHaen was used for the light-scattering study.

Cryogenic Study

Polymer solutions at concentrations ranging from 10^{-3} to 10^{-6} g/mL in THF and benzene were equilibrated at ambient temperature for several hours after preparation. Ten-milliliter samples were transferred into 2 cm diameter test tubes. Sealed test tubes were then immersed in liquid nitrogen for 2 min. All solutions were found to freeze completely within 1 min. The test tubes containing the solutions were removed from the liquid nitrogen container and thawed at room temperature or in warm water (30°–40°C) for 5 min.

Toluene solution of polystyrene with $M_p = 1.44 \cdot 10^7$ and $C = 5.8 \cdot 10^{-5}$ g/mL was subjected to cyclic treatments: 2 min liquid nitrogen freezing and subsequent 5 min 30°C thawing for 61 times. Both the original solution and the solution after freeze–thaw cycling were filtered with a 0.5-μm Millipore filter for light-scattering measurements.

Size-Exclusion Chromatography

All analyses were conducted with a Waters Associates GPC Model 210 equipped with RI R401 detector (for benzene as elution solvent), ultraviolet photometer Model 440 at the wavelength 254 nm (for tetrahydrofuran as elution solvent), Model 510 pump, and Data module 730 recorder. Narrow distribution standard polystyrene samples at concentrations of 10^{-4} g/g were used for calibration. Two column sets were employed. One consisted of μ-Styragel™ 10^4, 10^5, and 10^6 Å (Waters Assoc.) for the solvent tetrahydrofuran. The other consisted of μ-Bondagel™ E-500, E-1000, and μ-Bondagel™ E-High Å (Waters Assoc.) for the solvent benzene. The flow rate was kept at 1.0 mL/min at room temperature. An internal small molar mass standard was added into the sample solutions injected into the SEC column for correction of the flow rate.

Laser Light Scattering

A commercial laser light-scattering (LLS) spectrometer ALV/SP-125 was used with an argon ion laser operated at λ 532 nm and 400 mW as light source. All measurements were done at 25 ± 0.01°C in the range of scattering angle 20°–150°C. The *dn/dc* values of the original solution in toluene and the solutions after freeze–thaw cycling were determined at 25°C by a novel differential refractometer which was designed and constructed at the Chinese University of Hong Kong [16].

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