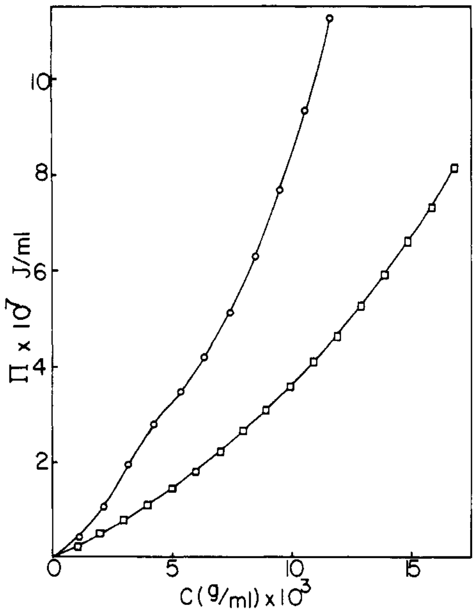

Figure 5. Plots of π vs. C (g/cm^3) of polystyrene in carbon tetrachloride at 25 °C (○) and in *trans*-decalin[6] at 40 °C (□).

40 °C. At infinite dilution, the ideal van't Hoff law holds. At $C < 1 \times 10^{-4}$ g/cm^3 $< C_1^*$, the π values are higher at higher temperatures and eq 8 remains valid. At higher concentrations, $C > 5.6 \times 10^{-4}$ g/cm^3 $> C_1^*$, the polymer segments are on the average uniformly distributed throughout the solution, and the Flory–Huggins theory[4] again predicts that the osmotic pressure increases with increasing temperature and concentration. In the intermediate concentration region, we have, in fact, observed a bump in the concentration dependence of the osmotic pressure.

V. Conclusions

Static and dynamical properties of polystyrene ($M_w \sim 1 \times 10^7$) in CCl_4 show the existence of an anomalous behavior between dilute and semidilute solutions. Near C_1^* we observed a change in the characteristic frequency, a decrease in the characteristic length, and a maximum in $(\partial\pi/\partial C)_{T,P}$. We visualize the polymer coil behavior between concentrations 1×10^{-4} and 5.6×10^{-4} g/cm^3 as individual (though not isolated) coils which are interpenetrable by neighboring coils without appreciable entanglement formation. The behavior is absent in fluid mixtures of small molecules, in polymer solutions under Θ conditions, and in a good solvent. It has been compared with the change of slope in heats of mixing and density of polymer solutions[7,8] in the intermediate concentration range and has been suggested incorrectly as a form of pseudotransition behavior.[9] The details of the metastable state in the intermediate concentration region will be reported in a separate article.

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Study of Thermal Polymerization of Styrene by Raman Scattering

B. Chu,* G. Fytas,† and G. Zalczer‡

Department of Chemistry, State University of New York at Stony Brook, Long Island, New York 11794. *Received May 22, 1980*

ABSTRACT: We present a new method for studying polymerization kinetics based on Raman scattering. Our method has selectivity, is reliable and easy to apply, can be automated, and is insensitive to most spurious phenomena. We demonstrate this method by a study of the thermal polymerization of styrene at 60, 75, and 90 °C.

Introduction

The thermal polymerization of styrene has recently been the subject of several studies by light-beating spectroscopy (polarized[1] and depolarized[2]), interferometry (polarized[3] and depolarized[4]), and NMR.[5] We present here a new method based on Raman scattering. Our method has selectivity, is reliable and easy to apply, can be automated, and involves little external calibration. We emphasize that, since polymerization involves changes in chemical bonds which can usually be observed through Raman lines, this technique should be applicable to almost any polymerization process.

Principle and Calibration

The principle of the method is to record Raman spectra from the sample at different stages of polymerization. In a polymerization reaction some portion of the molecular structure of interest usually remains unchanged. The corresponding Raman-active lines are present throughout the process and can be used as standards to calibrate the intensity of other lines, while those related specifically to the monomer vanish and those related to the polymer grow. Monitoring a ratio of intensities makes the measurement insensitive to laser power fluctuations or sample turbidity. Therefore, the method is reliable even in unfavorable conditions. In particular, applications of the method for studying copolymerization processes should be a worthwhile extension.

The first step is to measure Raman spectra of the monomer and of the polymer and to select the useful lines. When many Raman peaks are present, some of this in-

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[†] On a leave of absence from the University of Bielefeld, Faculty of Chemistry PC1, 48 Bielefeld 1, West Germany.

[‡] On a leave of absence from the Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay, SPSRM, BP 2, 91190 Gif-s/Yvette, France.

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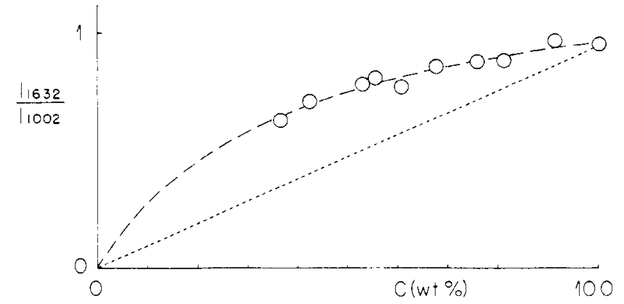

Figure 1. Ratio of the intensities of the 1632-cm^{-1} (double bond) line to the 1002-cm^{-1} (ring) line, I_2/I_1, as a function of the monomer concentration: (- - -) equal-scattering hypothesis; (— — —) fit to eq 2.

formation is redundant. Consequently, there is no need to scan the entire Raman spectrum during kinetic studies. Furthermore, for many interesting polymers the spectra and assignments of both the monomers and the polymers are available in the literature. In our case we selected the 1632-cm^{-1} line due to the aliphatic double bond (denoted by subscript 2) and the 1002-cm^{-1} line due to a ring vibration (denoted by subscript 1) for our studies of thermal polymerization of styrene. A natural hypothesis is to consider the ring lines independent of the concentration. In other words, the Raman scattering due to the ring vibration remains the same whether it belongs to a monomer or to a polymer. Unfortunately, *this is misleading.* Indeed we measured the ratio of those lines in polystyrene in styrene solutions of different known polymer concentrations. The above assumption predicts straight-line behavior, obviously not verified by the data, as shown in Figure 1.

Let c_m be the concentration of monomer molecules and c_p be that of polymer segments in a unit volume. The intensity due to the aliphatic double bond is $I_2 = a_2c_m$ and that due to the ring is $I_1 = a_1c_m + b_1c_p$, where $a_1 \neq b_1$. So we get

$$\frac{I_2}{I_1} = \frac{a_2c_m}{a_1c_m + b_1c_p} \tag{1}$$

If the concentrations appear only as ratios, we can use mass concentrations and normalize them so that $c_m + c_p = 1$. Then we have the empirical expression

$$\frac{I_2}{I_1} = \frac{a_2}{a_1}c_m\left[\frac{1}{b_1/a_1 + (1 - b_1/a_1)c_m}\right] \tag{2}$$

The equations are insensitive to density changes. The ratio a_2/a_1 is equal to I_2/I_1 when $c_m = 1$. The ratio b_1/a_1 can be deduced from a fit of the calibration data in Figure 1. The upper curve in Figure 1 represents a good agreement between eq 2 and our calibration using $a_2/a_1 = 1.32 \pm 0.06$ and $b_1/a_1 = 0.59 \pm 0.04$. The first of these ratios has a weak temperature dependence but the second, corresponding to lines at the same frequency, can be assumed constant and is essentially independent of the optical alignment of the Raman spectrometer. For more complex systems, other empirical formulas can be developed. In any case, a calibration is essential in order to achieve quantitative results.

Thermal Polymerization of Styrene

We have applied this technique to the thermal polymerization of styrene, using a Spex 1302 double-monochromator (0.5 m, 1200 grooves/mm) and recording the spectra by means of a chart recorder. As we were interested mainly in the integrated intensities of the peaks, we could use wide slits (~300 μm), which reduce the required laser power (~300 mW at 488 nm) and thence the occurrence of any photoactivated process. In fact, a spectrometer of much poorer quality would have been sufficient. On the other hand, refinements such as computer-controlled scan, digital recording, and automatic data acquisition can be introduced easily. We are in the process of making our experiments fully automatic.

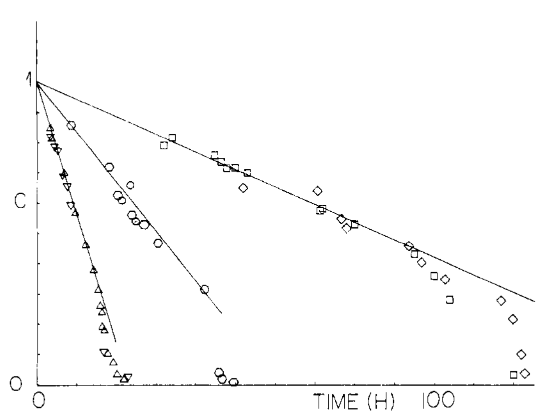

Figure 2. Concentration of monomer vs. time: (▽, △) cells 1 and 4, 90 °C; (○, ○) cells 2 and 5, 75 °C; (□, ◇) cells 3 and 6, 60 °C. H ≡ hour.

Table I

	temperature, °C		
	60	75	90
initial rate, %/h	0.32	1.1	3.1

Among the six samples we have studied, five were only degassed by several freeze–pump cycles, the inhibitor (*tert*-butylpyrocatechol) being left undisturbed. The sixth one was washed several times with water in order to remove the inhibitor and then dried, first with calcium chloride and then with calcium hydride. The observed rate of polymerization for that cell (no. 1) agrees quite well with the other measurements. We ran two samples at each of three temperatures, 60, 75, and 90 °C, and found good reproducibility in our measurements. The concentration of monomer vs. time is reported in Figure 2 for all cells. We find a linear behavior until about 65% of the reaction, where it suddenly becomes faster. Such a behavior, known as the Trammsdorf effect,[6] has been observed by light scattering techniques.[4] It is not clear yet whether this is a real phenomenon or an experimental artifact. Indeed when the viscosity of the sample becomes very high, the portion lighted is no longer renewed so the effect of several hundred milliwatts of light may no longer be negligible. In that region we have actually observed a thermal lens effect which has persisted hours after stopping the beam, but we cannot yet ascertain whether this effect is the reason for the change in the kinetics. Another possible reason for the acceleration in the polymerization kinetics is due to a decrease of the termination rate constant, in terms of intrachain interactions[6] and chain-transfer effect,[7] through tremendous viscosity increases during the polymerization process.

From the results of Figure 2, we can infer a variation of the initial rate with the temperature, as listed in Table I. The results are very well described by an Arrhenius law with an activation energy of 19 kcal/mol, the same as observed by classical methods,[8] as can be seen in Figure 3. On the other hand, the rates we found are about 3 times higher than usually reported. We believe this disagreement is possibly due to sample preparation procedures and not the observation method. In order to check the Raman detection method, we polymerized an additional styrene

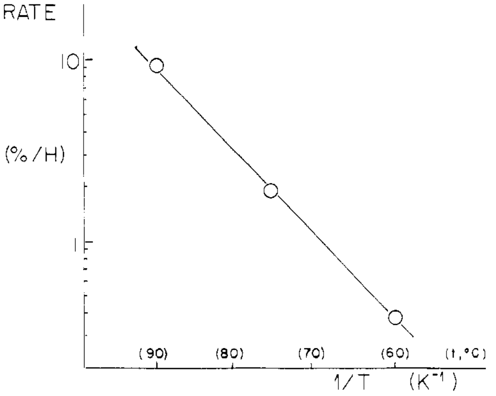

Figure 3. log of the initial reaction rate vs. reciprocal temperature. The solid line represents an Arrhenius law with an activation energy of 19 kcal/mol. H ≡ hour.

sample at 75 °C for 19 h, during which time we monitored the monomer concentration, as shown typically in Figures 1 and 2. After stopping the reaction, we determined the polymer conversion classically by first dissolving the polymerized sample in 1,4-dioxane and then precipitating the polystyrene in methyl alcohol.[8] We found an 18% conversion by the classical method and a 21% conversion based on Raman scattering. The agreement is quite reasonable, especially in view of the fact that there must be a residual amount of oligomers which are not precipitated by the classical method.

Conclusion

We have presented a new method for studying polymerization reactions based on Raman scattering. This method is fairly general, easy to use and to automate, and insensitive to most spurious phenomena. We have illustrated this method by a study of the thermal polymerization of styrene at different temperatures and found our results to be in essential agreement with those obtained by other methods.

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Phase Behavior of Reversibly Polymerizing Systems with Narrow Length Distributions

Judith Herzfeld*

Biophysical Laboratory, Harvard Medical School, Boston, Massachusetts 02115

Robin W. Briehl

Departments of Biochemistry and Physiology, Albert Einstein College of Medicine, Bronx, New York 10461. Received May 23, 1980

ABSTRACT: The lattice models of Flory and DiMarzio for rigid linear polymers of fixed length have been extended to describe reversibly polymerizing systems with narrowly distributed polymer lengths (i.e., it is assumed that the system remains approximately monodisperse as the average polymer length varies with concentration and other variables). Whereas irreversibly polymerized systems are expected to form a relatively dilute, partially aligned anisotropic phase unless sufficiently strong attractions between polymers are present to condense them, we find that reversibly polymerizing systems are expected to form a highly concentrated and highly ordered anisotropic phase unless sufficiently strong repulsions between polymers are present to separate them. The predicted temperature dependence of the phase behavior for the two systems is markedly different. For the reversibly polymerizing system there exists a temperature below which there is no phase transition at any concentration of solute. Just above this temperature there is a wide two-phase region in which a dilute isotropic phase, consisting of monomers or very short polymers, is in equilibrium with a quasi-crystalline phase consisting of very long, highly aligned polymers which essentially completely exclude solvent. The decrease in the concentration of the isotropic phase, with increasing temperature, occurs at a progressively decreasing rate to give an "elbow-shaped" phase boundary. The anisotropic phase remains very dense at high temperatures unless the interactions between polymers are sufficiently repulsive to separate them and admit solvent. The temperature dependence of the viscosity of sickle-cell hemoglobin solutions is consistent with the theoretical predictions. Interpretation of the experimental data in terms of the model suggests that domain dimensions could be a major determinant of the viscous properties of these sickle-cell hemoglobin solutions and could account for some of the hysteresis observed in these systems.

Introduction

If the axial ratio is large enough and the concentration high enough, long rodlike particles will align spontaneously, even in the absence of intermolecular interactions, as a consequence of excluded volumes. The theory for phase transitions of this type has been developed by Onsager,[1] Isihara,[2] and Zwanzig[3] for dilute solutions, using a virial expansion, and by Flory[4] and DiMarzio[5] for the full range

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