Appendix B

Criterion 15 for an extremum of the critical line can be transcribed as

$$\Gamma_{w\xi} + \frac{\partial\varphi}{\partial w_2}\,\Gamma_{\varphi\xi} + \frac{\partial\varphi}{\partial\xi^2}\,\Gamma_{w\varphi} = 0 \qquad \text{(B1)}$$

where $\Gamma_{\alpha\beta} \equiv G_\alpha K_\beta - G_\beta K_\alpha$. With the aid of critical eq 3, 5–6a, and 6c, this complicated expression can be simplified as follows: The partial derivatives of φ from eq 3 are

$$\frac{\partial\varphi}{\partial\xi^2} = 3\varphi(1-\varphi)w_1r_1w_2r_2\frac{r_2\xi^2 - r_1\xi^{-2}}{2\xi^2\langle r\xi\rangle\langle r^2\xi^3\rangle} \qquad \text{(B2)}$$

$$\frac{\partial\varphi}{\partial w_2} = \varphi(1-\varphi)\frac{(r_2^2\xi^3 - r_1^2\xi^{-3})\langle r\xi\rangle - 3(r_2\xi - r_1\xi^{-1})\langle r^2\xi^3\rangle}{2\langle r\xi\rangle\langle r^2\xi^3\rangle} \qquad \text{(B3)}$$

whereas the Γ terms obtained by taking derivatives of the critical functions G_c and K_c, eq 5 and 6a, can be rearranged into the forms

$$\Gamma_{w\xi} = -\boldsymbol{g}^{+}(r_2\xi^2 - r_1\xi^{-2}) \qquad \text{(B4)}$$

$$\Gamma_{\varphi\xi} = \boldsymbol{g}^{+}w_1w_2(r_2\xi^2 - r_1\xi^{-2})(r_2\xi - r_1\xi^{-1})/(\varphi\langle r\xi\rangle) \qquad \text{(B5)}$$

$$\Gamma_{w\varphi} = 4\xi\ (\mathrm{d}\xi/\mathrm{d}\eta)\ \boldsymbol{g}^{+}(r_2\xi^2 - r_1\xi^{-2})/(\varphi\langle r\xi\rangle) \qquad \text{(B6)}$$

where $\mathrm{d}\xi/\mathrm{d}\eta$ is specified by eq 21. After the quantities defined above are substituted in eq B1, the common term

$$\boldsymbol{g}^{+}(r_2\xi^2 - r_1\xi^{-2})(1-\varphi)/(\langle r\xi\rangle\langle r^2\xi^3\rangle) \qquad \text{(B7)}$$

can be factored out, and the two products of differences of $r_i^m\xi^n$ terms appearing in the second term of eq B1 can be expressed as differences of moments from the formula

$$w_1w_2(r_2^m\xi^n - r_1^m\xi^{-n})(r_2^{i-m}\xi^{j-n} - r_1^{i-m}\xi^{n-j}) = \langle r^i\xi^j\rangle - \langle r^m\xi^n\rangle\langle r^{i-m}\xi^{j-n}\rangle \qquad \text{(B8)}$$

This operation and some subsequent rearrangement finally make the residue identical with criterion 17.

The extremal condition for the critical line thus leads in fact to the product of two criteria as expected: one for a HODCP contained in the factor (B7) (cf. eq 11); the other for a HEDCP remaining in the residue.

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Microphase Formation in Solutions of Diacetylene-Containing Segmented Block Copolymers

Rong-Chang Liang,† Wen-Yih Frank Lai, and Arnost Reiser*

Institute of Imaging Sciences, Polytechnic University, Brooklyn, New York 11201.

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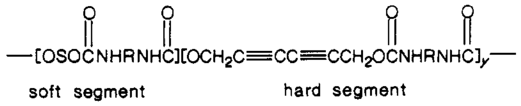
ABSTRACT: In solutions of the diacetylene-containing segmented block copolymers described earlier, micelles are formed which consist of a compact hard segment core surrounded by a less dense shell of soft segment. The diacetylene units are built into the hard segments and can polymerize only in more or less ordered aggregates. Micelle formation can, therefore, be monitored by the appearance of the characteristic purple color of the polydiacetylenes. The effect of polymer concentration and of solvent composition on micellization is investigated, and the criteria for the formation of unimolecular and multimolecular micelles are considered. The kinetics of the micellization process are characterized by an activation energy of 3.7 kcal/mol. An estimate of micelle size is obtained by gel permeation chromatography. The overall size of the micelles in the early stages of microphase formations is estimated at 180 Å.

Earlier we reported on the photoreactivity of diacetylene-containing block copolymers.[1,2] The photoreactivity of these materials depends on the degree of phase separation between a predominantly hard segment microphase and a predominantly soft segment continuum. It also depends on the size and the degree of order in the diacetylene stacks of the hard segment phase. This molecular morphology which determines the photochemical behavior of the solid is preformed in polymeric micelles while the system is still in a fluid state. The present paper is concerned with the formation of micelles in solutions of diacetylene-containing block copolymers.

Our investigation was conducted on copolymers of the general composition



$$-[\mathrm{OSO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHRNH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}][\mathrm{OCH_2C{\equiv}CC{\equiv}CCH_2O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHRNH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}]_y-$$

Here R stands for $-(CH_2)_6-$, S stands for $-(CH_2)_5CO-$, the hard segment content is either 35% or in some cases 25%,

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† Present address: Mead Imaging Inc., Miamisburg, OH 45342.

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the molecular weight of the soft segment component is 2000 or 1250, the index y is 5.2, and the weight-average molecular weight of the block copolymer is about 60 000. In earlier communications, these polymers were identified by the acronyms HDI-PCL-35-2000, HDI-PCL-25-2000, HDI-PCL-35-1250, etc., where the first number (e.g., 35) indicates the hard segment content in weight percent, and the second number (e.g., 2000) indicates the molecular weight of the soft segment.

Transmission electron micrograms of thin films[3] of the materials had shown microdomains of approximately spherical shape in both unirradiated and irradiated samples. It was thought that these domains were in the nature of spherulites, agglomerations of polymeric micelles formed in the casting solutions.[4]

The occurrence of micelles in solutions of segmented block copolymers in general was first reported by Krause.[5] Kotaka et al.,[6] Tuzar and Kratochvil,[7] and others have made important contributions to the subject, and Gallot[4] has written an excellent review. More recent work by Shibayama et al.,[8] Noolandi,[9] Leibler,[10,11] and Roe[12,13] must be mentioned.

In the case of the diacetylene-containing polymers, the formation of micelles is a precondition for photoreactivity: irradiation of very dilute solutions in good solvents for both the hard segment and the soft segment component produces no change in the system. However, at a critical concentration (e.g., 0.3% polymer in THF), the characteristic purple color of the polydiacetylenes appears. The polymerization of diacetylenes occurs only in ordered molecular stacks and requires therefore the aggregation of a number of diacetylene units in a compact space. The photoreaction is proof of the formation of micelles.

Since diacetylene polymerization requires the formation of hard segment aggregates from which the soft segments are largely excluded, the micelles are thought to consist of a compact diacetylene-containing hard segment core, surrounded by a less dense soft segment shell or corona (see ref 11) which acts as a protective colloid. Tuzar et al.[14] have shown that in similar circumstances, micelles of this kind are formed in a number of common block copolymers.

The micellization process may occur in two different ways. At very low concentration and in a good solvent, the polymer is dispersed in the form of random coils, the so-called unimers.[15] Here, the diacetylene units are not in contact, and consequently, the system is not sensitive to radiation. At a certain concentration, the equilibrium solubility of the hard segment component is exceeded in solution and, in these conditions, the individual macromolecules may form *unimolecular* micelles. The concentration of incipient micellization is termed the critical micelle concentration (cmc). However, if the solubility of the hard segments in the solvent is high, the coils of the dissolved polymer will interpenetrate before the cmc is reached, and eventually, at the critical micelle concentration, *multimolecular* micelles are formed. The presence of multimolecular micelles in many of our systems is indicated by the fact that irradiation of solid films cast from the same material produces intermolecular cross-links, as described earlier.[1]

We have investigated the process of micelle formation as a function of polymer concentration and of solvent composition and as a function of time and of temperature, and we have obtained an estimate of the size of the micelles.

Experimental Section

The synthesis of the block copolymers was described earlier.[16]

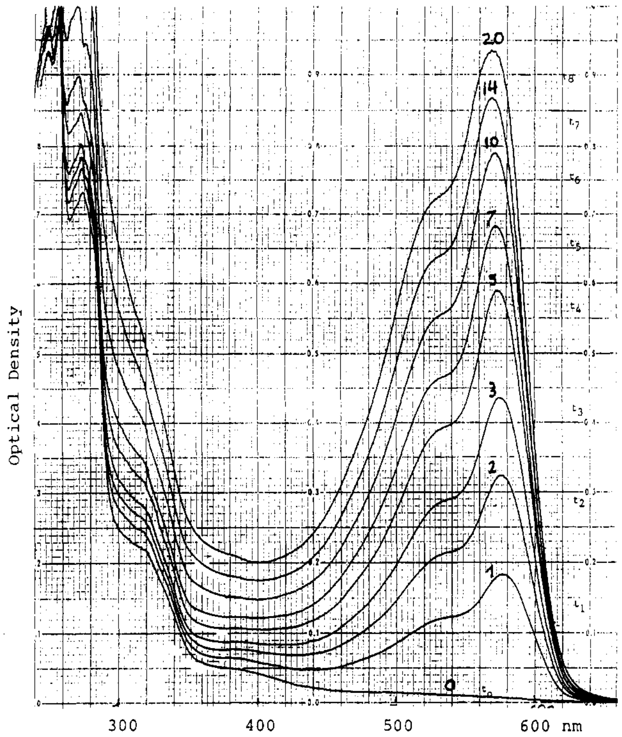

Figure 1. Time evolution of absorption spectrum of a 0.3% solution of HDI-PCL-35-2000 in THF irradiated at room temperature with 254-nm radiation. The numbers on the individual traces indicate irradiation times in minutes. Density scale: 0–2.0.

The molecularly dispersed solutions were prepared by refluxing the required amount of the polymer with solvent for about 10 min, together with 200 ppm of an antioxidant, butylated hydroxytoluene (BHT). The solutions were then cooled to room temperature under constant stirring and could be stored overnight at 10 °C without any changes occurring.

The solutions were irradiated in spectrophotometric quartz cells. The radiation source was a low-pressure mercury lamp emitting almost exclusively at 254 nm.

The formation of polydiacetylenes was monitored with a Cary 19 spectrophotometer in terms of the optical density of the solution at 580 nm. Figure 1 shows typical spectrometer traces taken at intervals during irradiation.

The appearance of micelles was also monitored by turbidimetry. For that, cylindrical cells with 100-mm path length were filled with the solutions, and the apparent optical density was measured at 650 nm, well outside the absorption of polydiacetylenes. Turbidity is normalized to a 1-cm path length: $\tau = D(650)/10$.

Gel permeation chromatograms of the solutions were run on a Waters chromatograph fitted with five columns in series; two had pore sizes of 500 Å, two pore sizes of 10^4 Å, and one a pore size of 10^5 Å. Detection was by IR and by UV monitors. The elution volume scale was calibrated in terms of molecular weight with a set of monodisperse polystyrenes.

Results and Discussion

Monitoring Micelle Formation by the Diacetylene Photoreaction. The polydiacetylene absorption band at 580 nm is a sensitive monitor of the photoreaction.[1,3] The rate of change of the optical density is given by

$$\mathrm{d}D(580)/\mathrm{d}t = \epsilon(254)r(10^3)I_a(254)\phi$$

Here $\epsilon(254)$ is the molar extinction coefficient of the diacetylene chromophore at the wavelength of irradiation, r is the optical path length of the spectrometer cell (1 cm), ϕ is the quantum yield of polymerization, and I_a is the radiation intensity absorbed by the chromophore. In the early stages of irradiation and in moderately concentrated solutions ($c > 0.05\%$), all the incident radiation (I_0) is absorbed, $I_a = I_0$, and the initial value of the rate of change of optical density is a true measure of the initial quantum

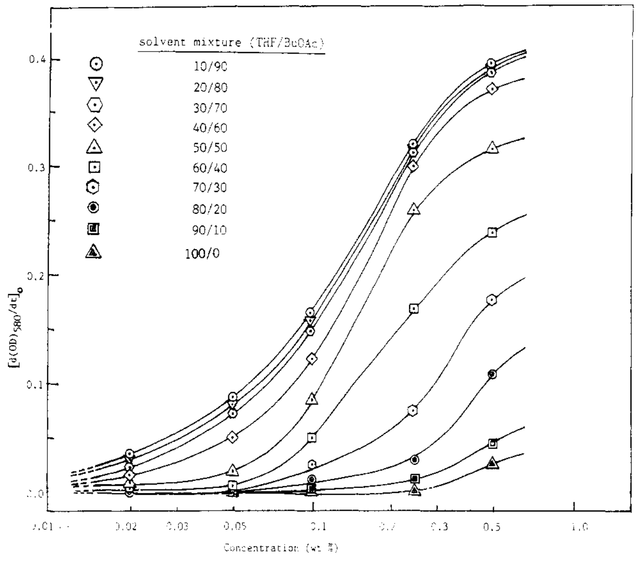

Figure 2. Initial rate, R_0, of diacetylene photopolymerization as a function of polymer concentration for a range of solvent compositions. Polymer: HDI-PLC-35-1250.

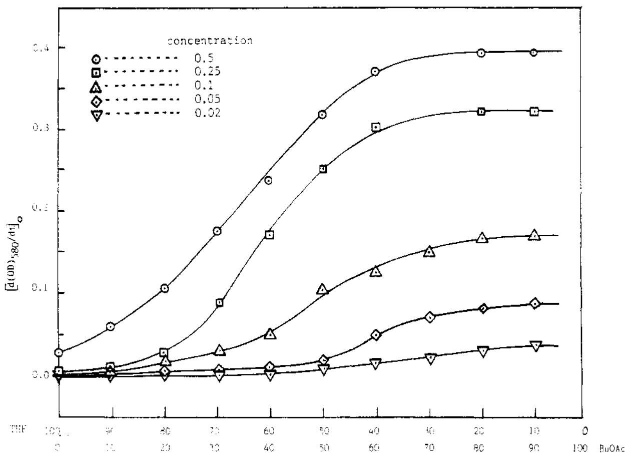

Figure 3. Initial rate of diacetylene photopolymerization as a function of solvent composition for a number of polymer concentrations. Polymer: HDI-PCL-35-1250.

yield of diacetylene polymerization. This in turn depends on the average number of diacetylene units in the molecular stacks and hence on the average size of the hard segment core of the micelles.

The initial rate of change of the optical density, R_0, is plotted in Figure 2 as a function of polymer concentration for a range of solvent compositions and in Figure 3 as a function of solvent composition for a number of polymer concentrations. It can be seen that the critical micelle concentration (cmc), which is indicated by a rise in R_0, decreases in parallel with the strength of the mixed solvent. In these experiments, we have used mixtures of THF and butyl acetate. THF is a good solvent for both components; butyl acetate is a good solvent only for the soft segment and merely a diluent for the hard segment. Consequently, solvent strength for the hard segment decreases with decreasing THF content in the mixture.

Whether unimolecular or multimolecular micelles are formed depends on the state of the solution at the cmc. If the macromolecular coils are interpenetrated at that point, multimolecular micelles result. This criterion can be expressed in terms of the deGennes critical concentration, c^*, which divides dilute from semidilute solutions and which marks the beginning of coil interpenetration. Multimolecular micelles are formed when cmc is larger than c^*.

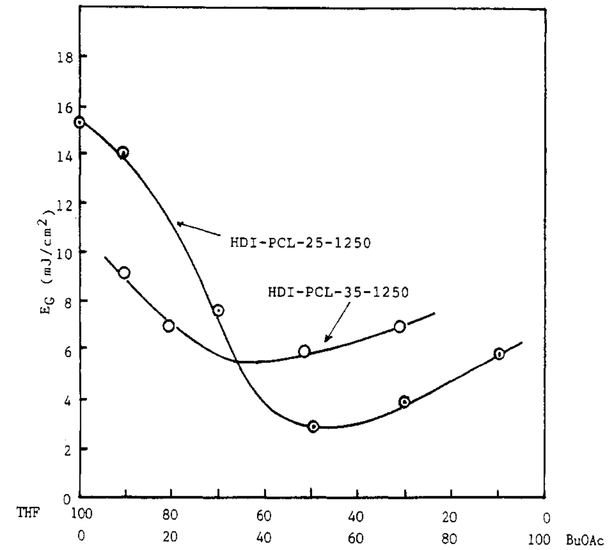

Figure 4. Effect of initial composition of casting solvent on the gel dose of polymer films. Polymers: HDI-PCL-25-1250 and HDI-PCL-35-1250.

Chang and Morawetz[19] have shown recently that the critical concentration, c^*, is inversely proportional to the inherent viscosity of the solution and hence inversely proportional to coil volume:

$$c^* \sim 1/[\eta] \propto M/\text{coil volume}$$

Since the coil volume decreases, the critical concentration will increase with decreasing solvent strength. In mixtures of THF and butyl acetate, that means that c^* will increase with increasing content of BuAC, while in the same conditions cmc will decrease. In going from pure THF to BuAc, there will come a point where cmc will be smaller than c^* and where therefore unimolecular micelles will be formed.

Indirect support for this comes from the dependence of the quantum yield of *intermolecular* cross-link formation on the composition of the casting solvent. This is shown in Figure 4. While the rate of overall (intermolecular and intramolecular) cross-link formation (monitored by the change in optical density at 580 nm) increases steadily with the content of BuAc, the efficiency of intermolecular cross-link formation (which can only occur in multimolecular micelles) reaches a maximum at 40–50% BuAc and then decreases as the intramolecular reaction gradually overtakes the intermolecular process. It must be emphasized that the data of Figure 4 are at present not amenable to quantitative analysis, but we nevertheless believe that the behavior observed in our systems is caused by a change from intermolecular to intramolecular cross-linking. More work needs to be done before the effect of the initial composition of casting solvents on the phase structure of cast films of block copolymers can be quantitatively understood.

Monitoring Micelle Formation by Turbidimetry. Micelle formation was also monitored by turbidimetry. The results are slightly different from those obtained with the photochemical probe because the two methods are based on different phenomena. The initial rate, R_0, of the photoreaction is linked to the size of the diacetylene stacks in the hard segment core; turbidity, on the other hand, measures the light-scattering power of the whole micelle, including the soft segment shell. In general, the photoreaction is a more sensitive indicator of incipient micelle formation, as can be seen in Figure 5, where R_0 and the turbidity are plotted as a function of solvent content for the polymer HDI-PCL-35-1250.

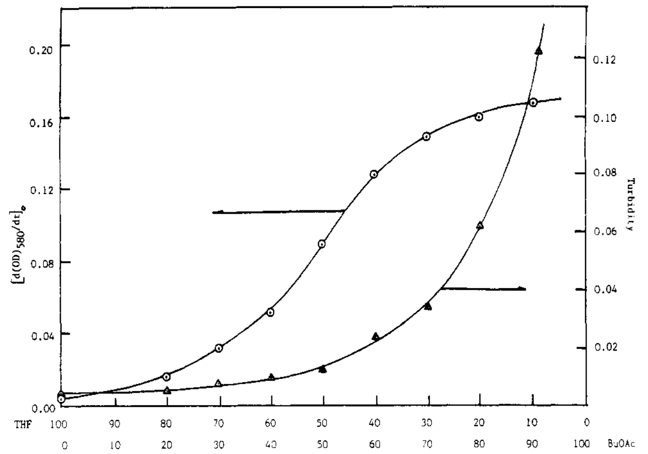

Figure 5. Effect of solvent composition on the initial rate of diacetylene photopolymerization and on solution turbidity, in 0.3% solutions of HDI-PCL-35-1250.

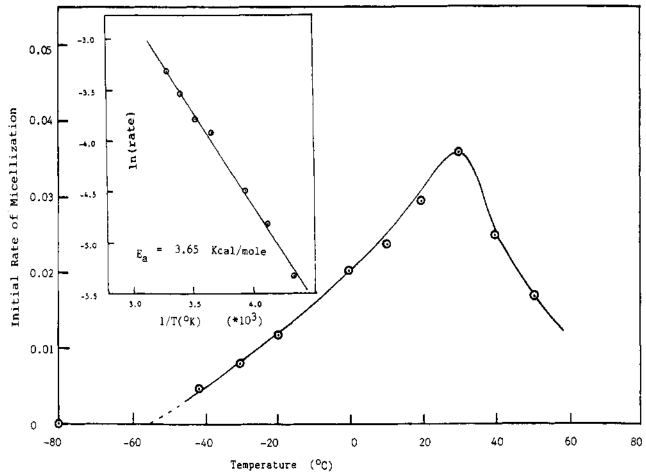

Figure 6. Dependence of initial rate of micelle formation on temperature for 0.3% HDI-PCL-35-2000 in THF. Inset: Arrhenius plot of logarithm of micellization rate vs. $1000/T$. The activation energy is $E_a = 3.7$ kcal/mol.

It will also be noted that while the scattering power increases monotonously as the micelles agglomerate into larger particles, the initial rate, R_0, levels off at low solvent strength, because the micelles, once formed, do not fuse their hard segment cores on aggregation.

Kinetics of Micelle Formation. Micelle formation in general is a slow process.[8] In our systems, the time evolution of the micelles can be followed by turbidimetry or via the photoreaction of the diacetylenes. To do that, the solutions were prepared as described before and then kept under constant stirring at a given temperature. Samples were taken at set time intervals and irradiated, and the initial rate of polymerization, R_0, was determined. In a parallel sample, the turbidity was measured in the usual way. If the experiment is repeated at different temperatures, the activation energy of the micellization process can be determined. Figure 6 shows the effect of temperature on the initial rate of micellization. Up to a temperature of 30 °C, the rate of micellization increases with increasing temperature. In this range, the process is controlled by kinetics, and the data give a linear Arrhenius plot (see insert in Figure 6), with an activation energy of 3.7 kcal/mol. This is an appropriate value. The slow rate of micellization is caused primarily by the negative activation entropy associated with the reorganization of the free coil into a compact micelle. The activation barriers of the process are, however, quite low, being linked to the rotational realignment of saturated C–C bonds, which have rotameric potential energy barriers in the range 2–5 kcal/mol.

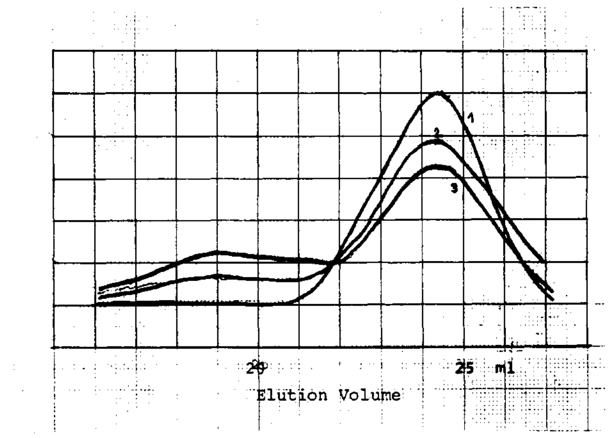

Figure 7. Gel permeation chromatograms of HDI-PCL-35-2000, 0.25% in THF. Injection volumes, 200 μL; UV detector; flow rate, 1.0 mL/min; (1) freshly dissolved polymer, (2) polymer injected after holding solution 30 min at room temperature, (3) polymer irradiated after holding solution 30 min at room temperature and then injecting into column.

Above 30 °C, the kinetic barriers are overcome and the reaction is now controlled by thermodynamics. In that range, increasing temperature shifts the equilibrium

$$\text{free coil} \rightleftarrows \text{ordered stacks (micelle)}$$

in the direction of the free coils and hence toward a lower concentration of reactive centers in the system.

Estimate of Micelle Size. The slow kinetics of micelle formation and micelle dispersion make it possible to estimate micelle size by gel permeation chromatography. Spacek and Kubin[18] have introduced this method recently and demonstrated it on a poly(butene-*co*-styrene) block copolymer. We have followed a simplified procedure.

The polymer, in this case HDI-PCL-35-2000, was dissolved completely in THF to a concentration of 0.25%, and a sample of the solution was immediately injected in a Waters GPC column. The column was in five parts with pore sizes 2 × 500 Å, 2 × 10^4 Å and 1 × 10^5 Å. Injection volumes were 200 μL; the flow rate of the eluent (THF) was 1.0 mL/min.

A second sample of the solution was taken half an hour after the solution had been made up. It was injected as before. A third sample was taken at the same time, irradiated with 254-nm radiation, and then injected. The intention was to fix the micelles by cross-linking the hard segment core. The three chromatograms are shown in Figure 7.

Before injection, all samples were filtered through a Millipore filter of pore size 0.5 μm. It was found that the quantity of unfiltrable material increased sharply with polymer concentration, in particular if this concentration exceeded c^*. It appears that in these systems, the micelles were interconnected by fibrilles formed from macromolecules belonging to two or more micelles at the same time. We have tried to chose our experimental conditions such as to minimize this effect.

While the first sample has only one peak at an elution volume of 24.4 mL, which corresponds to the elution volume of individual macromolecules (unimers), the second and third samples are bimodal and have a distinct second peak at about 19-mL elution volume. This second peak belongs to the multimolecular micelles which have formed in the solution during the 30-min wait. It can be seen that the irradiated sample has a stronger second peak; the micelles have grown a little further during the time of irradiation. The position of the second peak is similar in the second and third samples and allows an estimate to be made of the molecular weight of the micelles.

From a calibration of the column with a set of monodisperse polystyrene samples, one finds that the viscosity-average molecular weight of the free polymer molecules is 43 000; that of the micelles is abut 350 000. The average number of macromolecules per multimolecular micelle is therefore 350:43 = 8. This value is in good agreement with the quantum yield of cross-link formation, $\Phi = 9$, measured in films of the same material cast from THF solution.[1] It will be recalled that the quantum yield of intermolecular cross-link formation measures in effect the number of polymer chains taking part in the average diacetylene stack of the solid film.

From these data and from the composition of the polymer, the volume of the micelle core is estimated to be of the order of 1×10^{-18} cm^3, corresponding to an inner core diameter of about 100 Å. The overall micelle volume is estimated at 6×10^{-18} cm^3, corresponding to an outer micelle diameter of 180 Å.

Registry No. $(HDI)(HOCH_2C{\equiv}CC{\equiv}CCH_2OH)(CL)$ (copolymer), 109960-52-3.

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Polycondensation of Methyltrimethoxysilane

K. A. Smith

Research & Development Center, Corporate Research & Development, General Electric Company, Schenectady, New York 12301.

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ABSTRACT: Kinetics of the hydrolysis and self-condensation of methyltrimethoxysilane in organic–water (acetone-d_6 or CD_3CN) solvent systems were studied. The specific acid-catalyzed hydrolysis was found to be first order in substrate. By ^{29}Si NMR techniques, condensation was monitored and modeled by a set of propagation and condensation reactions. The solution to this set of equations indicates that hydrolysis of methyltrimethoxysilane and condensation of partially hydrolyzed methyltrimethoxysilane have competitive rates. Reactions between condensed species are on the average 17 times slower than condensations involving partially hydrolyzed methyltrimethoxysilane. Further characterization of condensation was attempted by using a statistical model with kinetic constraints. This approach was shown, in the limit reached by assuming diffusion between all sites, to be the same description obtained by the finite difference solution to a set of rate expressions for propagation and condensation processes. The molecular weight distribution as a function of the extent of reaction, as well as the gel point, was deduced from the model, and the dependence of the latter on attributes of the model is discussed.

Introduction

The hydrolysis and condensation chemistry of alkoxysilanes (or silanols derived from them) has been studied extensively.[1-4] The more quantitative investigations have, in general, been concerned with hydrolysis[1] owing to the relative simplicity of this process compared to condensation, particularly polycondensation of di-, or tri-, or tetraalkoxysilanes. This is not to imply that descriptions of the polycondensation chemistry of these systems have not appeared in the literature. Indeed, ceramic literature contains several examples of studies of tetraalkoxysilane hydrolysis and condensation.[2] Although analogous work on difunctional compounds has been reported,[3] comparable studies of trialkoxysilanes are rare.[4]

$$n\mathrm{CH_3Si(OCH_3)_3} + 1.5n\mathrm{H_2O} \xrightarrow{\mathrm{H+}} \text{polysiloxanes} + 3n\mathrm{CH_3OH} \quad (1)$$

where for complete reaction, polysiloxanes = $[\mathrm{CH_3SiO_{1.5}}]_n$

The role of trialkoxysilanes in resin synthesis, in addition to their place in elastomer technology, led to the experiments described herein. The concerns of relative hydrolysis and condensation rates (eq 1) of methyltrimethoxysilane (MTMS), the simplest alkyltrialkoxysilane, as well as the general question of how to model this polycondensation process, were foremost in our minds and are the focal points of this study.

Results and Discussion

Hydrolysis Studies. The hydrolysis of MTMS catalyzed by *p*-toluenesulfonic acid (*p*-TSA) in acetone was followed by GC analysis, as well as ^1H NMR spectroscopy. These experiments found hydrolysis to be first order in substrate under conditions of excess water (11 equiv)—plots of ln [MTMS] versus time being linear ($r > 0.99$) for greater than three half-lives. This dependence, in conjunction with the absence of dimer 1,1,3,3-tetramethoxy-1,3-dimethyldisiloxane (**1**) as a product, suggests that MTMS does not undergo a competitive condensation reaction with initially formed hydrolysis products. An additional verification of this conclusion was the demonstration that **1** hydrolyzes 16 times more slowly than