porphyrins. However, the S/HDA copolymers show an increase in molecular weight with decreasing HDA feed concentration (increasing reaction time). Earlier samples in the S/HDA copolymerization have a very high weight fraction of HDA in the copolymer and a large number of hemins per chain.

Conclusions

Iron protoporphyrins without strong axial ligands, such as HDME in the Fe(II) and Fe(III) state, appear to retard polymerization through reactions of a radical with the iron atom via redox reactions. The retardation is seen in the very slow rate of conversion for these copolymers in comparison with pure polystyrene. Ligands such as carbon monoxide, cyanide, and 1-methylimidazole prevent the reaction of a radical with the central iron and allow polymerization to proceed in a usual manner. The molecular weight of a heme/styrene copolymer with a carbon monoxide ligand remains constant, despite varying heme concentration, which suggests that heme is not a chain-terminating agent and is incorporated in the polymer chain.

Protoporphyrins are very reactive vinyl monomers owing to the conjugation with the porphyrin ring. This may be seen in the considerable enrichment of iron porphyrin in the polymer composition from the monomer feed. Thus one would expect a relatively slow rate of polymerization. This is seen in the S/HDA case, where the polymer is composed of a significant amount of hemin and the rate of conversion is slower than those polymerizations where the iron porphyrin enrichment is less significant. Also it appears that Fe(III) hemins polymerize more slowly and are more reactive monomers than Fe(II) hemes, possibly due to the greater resonance stabilization of the radical. This is observed in comparing the slower rate of conversion of S/HDME·$(CN)_2$ to those of S/HDME·CO and S/Fe^{II}HDME·$(IM)_2$.

We have postulated a mechanism of hemin enrichment observed in the S/HDA polymerization where the axial basis of the HDA, in solution or at the end of a polymer chain, may bind to nearby hemins. The physical proximity of these monomers results in an increased probability of hemin–hemin polymerization over hemin–styrene copolymerization. We have shown that when one of these ligands is displaced, as in the S/Fe^{II}HDA·CO polymerization, the reaction proceeds as a usual styrene–heme copolymerization.

Registry No. S/Fe^{II}HDME·CO, 85166-72-9; S/Fe^{III}HDME·$(CN)_2^-$, 85166-73-0; S/Fe^{II}HDME·$(IM)_2$, 85185-10-0; S/Fe^{III}HDA, 85166-75-2; S/Fe^{II}HDA·CO, 85166-77-4; S/Fe^{II}HDME, 78035-29-7; S/Fe^{III}HDME, 85166-78-5.

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Energetics of Diacetylene Photopolymerization: A Calorimetric Study

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ABSTRACT: A detailed calorimetric study is presented for the photopolymerization of a highly radiation-sensitive diacetylene. The polymerization kinetics, heat of polymerization, and quantum yield are presented and compared to photoacoustic studies of the same diacetylene compound. The quantum yield is very high (~125), in good agreement with the photoacoustic results. The heat of polymerization is 0.95 eV per monomer unit, a value that is considerably lower than the value derived from previous thermal polymerization studies of other diacetylenes. We conclude from these results that the energetics of diacetylene solid-state polymerization are influenced by differences in side-group interactions. An unfavorable side-group interaction in the polymer vs. the monomer leads to a decreased heat of polymerization, higher photopolymerization quantum yields, and a high activation energy for thermal polymerization. Favorable polymer side-group interactions are predicted to show the opposite behavior.

I. Introduction

Over the past few years differential scanning calorimetry (DSC) has been used to study basic photoinitiated polymerization phenomena, including polymerization kinetics for various photocurable polymer systems.[1-3] These photocurable systems are mainly used for coatings and printing inks. DSC is especially suited to study photopolymerization kinetics because the rate of the reaction can be measured directly and only small samples are required.

We have utilized the technique of photocalorimetry to study the UV-induced solid-state polymerization of a diacetylene. The solid-state reaction of diacetylenes can be initiated by thermal annealing,[4] pressure, UV,[5] high-energy

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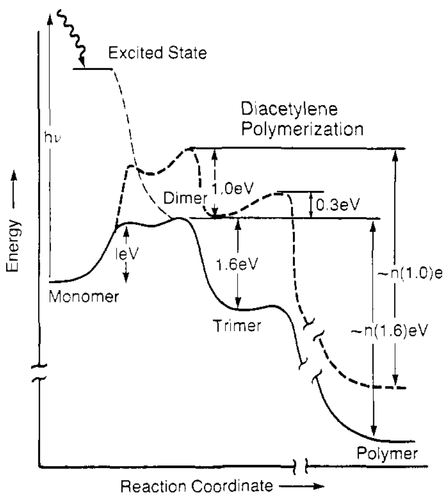

Figure 1. Reaction diagram for the thermal polymerization and photopolymerization of diacetylenes: solid curve, energetic parameters taken from ref 9 for a thermally polymerized diacetylene; dashed curve; energetic parameters from present work (photopolymerization of 4BCMU).

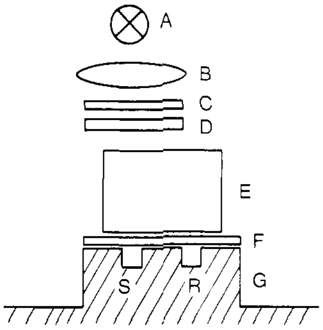

Figure 2. Schematic diagram of modified Perkin-Elmer DSC-4: (A) light source; (B) focusing optics; (C) light shutter; (D) interference filter; (E) quartz cell filled with water; (F) sapphire cover plate; (G) DSC head; (S) DSC sample cell; (R) DSC reference cell.

radiation,[6] or exposure to certain gases;[7] the polymerization is a prime example of a lattice-controlled solid-state reaction. Calorimetric studies of the thermal polymerization of crystalline 2,4-hexadiyne-1,6 diol bis(*p*-toluenesulfonate) (PTS)[8,9] demonstrate that the polymerization is strongly exothermic and temperature activated by about 1 eV. This activation energy, E_a, should be roughly the energy difference between the monomer and the dimer intermediate to chain propagation. The dimer either returns to the monomer ground state with high probability or starts a chain propagation event. Each propagation step, i.e., addition of a monomer unit to the chain in PTS, releases ~1.6 eV. Recent ESR experiments support this scheme and identify the intermediate to chain initiation as a biradical dimer.[10,11]

In the photopolymerization process, the activation barrier is overcome by the photon energy. The monomer excited state reacts with a monomer ground state to form the biradical dimer, which can then initiate the chain as in the case of the thermal polymerization. Since the activation energy for UV polymerization of PTS measured near room temperature is quite small (0.1 eV),[5] the activation energy E_a = 1 eV for thermal polymerization is primarily associated with chain initiation and not with the chain propagation event. The energetics of these processes are illustrated in Figure 1. Also of interest in the photopolymerization process is the quantum yield, defined as the number of poly(diacetylene) repeat units produced per absorbed photon. This quantity is usually written as the product nq, where n is the chain propagation length in polymer repeat units (ru) and q the chain initiation probability. A wide range of values for the quantum yield has been reported in the literature for various diacetylenes.[5,12]

Photoacoustic (PA) spectroscopy has recently been used in a calorimetric study of the reaction kinetics of a highly radiation-sensitive diacetylene, $RC{\equiv}C{-}C{\equiv}CR$, where R is $(CH_2)_4OCONHCH_2COOC_4H_9$.[12] This compound, 4BCMU, though quite UV reactive, shows virtually no thermal reactivity. These PA experiments convincingly demonstrate the exothermic nature of the photopolymerization process. In a PA experiment the heat evolved as a result of a photochemical reaction as well as that due to photon absorption is detected by a microphone located in the gas surrounding the diacetylene crystal or by a piezoelectric transducer attached to the back of the crystal. Therefore, a crucial aspect of these experiments is the efficiency of heat detection, i.e., the acoustical coupling of the crystal to the surrounding gas and/or the heat transfer through the solid. The photochemical heat evolved scales as $nq\Delta H_p$, where ΔH_p is the heat of polymerization in units of energy per polymer repeat unit (ru). In a first analysis of the PA data Chance and Shand[12] estimated a quantum yield of eight polymerized units per absorbed photon assuming a heat of polymerization ΔH_p = 1.6 eV/ru derived from thermal polymerization experiments with PTS. Later Prock et al.[13] presented a more detailed experimental study and a more complete theoretical description using a one-dimensional heat-diffusion model which explicitly considers the efficiency of acoustical coupling between the gas and solid. The latter intepretation gave a quantum yield of nq ~100 (taking ΔH_p = 1.6 eV/ru) and required that the polymer couples acoustically much more effectively to the gas than does the monomer.

In this paper we report the first direct determination of ΔH_p for the photopolymerization of a diacetylene. We show that the assumption of a single ΔH_p value for diacetylene polymerization is not valid, a confirmation of previous work.[14] We also demonstrate advantages of DSC over PA in the study of photochemical reactions.

II. Experimental Section

A Perkin-Elmer DSC-4 was modified to allow irradiation of the sample in the DSC chamber (see Figure 2). The swing-away cover was replaced by sapphire cover plates. A cylindrical quartz cell filled with water was placed above the sample pan to filter any infrared radiation. Neutral-density filters could be inserted in the light path to reduce the intensity. Either a 50-W deuterium lamp with a 260-nm, 10-nm-band-pass interference filter and a Corning 7-54 UV filter or a 150-W xenon arc lamp with a Schoeffel GM 100 monochromator was focused on the sample. The light could be blocked by a shutter. No UV light was allowed to strike the reference cell. The DSC was calibrated by the heat of fusion of indium (6.80 cal/g). A Perkin-Elmer 3600 Data Station was employed to acquire the data and store them on floppy disks. All measurements were done isothermally at 50 °C. Integration of the DSC curves to obtain ΔH_p was done with the Perkin-Elmer TADS software. The integration was started just before the light was incident on the sample and concluded after the light was blocked and the signal had returned to the base line. The ΔH_p values were found to be independent of instrument time constant and measurements were routinely performed with the fastest time constant. When necessary the calorimetric signal was output on a HP 7047A X-Y recorder for higher sensitivity and faster response.

We choose the diacetylene 4BCMU, R = $(CH_2)_4OCONHCH_2COOC_4H_9$, for this investigation for several reasons: (1) the monomer is highly radiation sensitive but shows no significant thermal reactivity up to its melting point (74 °C), (2) the polymer

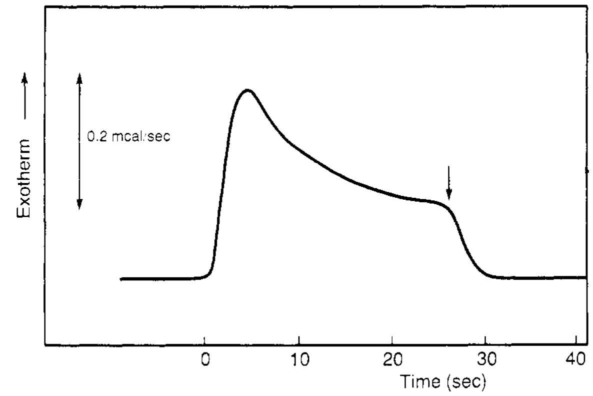

Figure 3. Typical DSC trace for photopolymerization; $t = 0$ denotes beginning of irradiation; the arrow denotes the end of irradiation.

is soluble in common organic solvents, which allow the easy and accurate determination of the polymer content after irradiation, and (3) the same compound was used in the photoacoustic calorimetry experiment, thus allowing direct comparison of the results obtained by the two methods.

All experiments discussed here were done either on 4BCMU powders (between 1 and 5 mg) or on thin films obtained by melting the powder in the DSC sample pan and cooling the compound down to 50 °C. 4BCMU turned dark blue within seconds after the opening of the light shutter. The amount of polymer after irradiation was determined by dissolving the powder (or film) in 10 mL of $CHCl_3$ and measuring the absorbance of the polymer solution ($\epsilon_{max} = 17000$ L/mol cm at 470 nm) with a Perkin-Elmer 330 spectrophotometer controlled by the same Data Station. This method was shown previously to give accurate values for polymer conversions.[15] Conversions were typically in the range 1–5%. Corrections were made for the small amount of polymer present in the unirradiated powders (typically <0.1%).

To test our experimental setup and to ensure that all the heat evolved during a chemical reaction was collected by the DSC apparatus, we repeated the calorimetric study of the isothermal polymerization of PTS in our experimental configuration, i.e., with an open pan. PTS monomer (4.8 mg) was introduced into the DSC, which was set at 90 °C. The DSC signal was recorded for 140 min, a time period long enough to ensure complete polymerization at this temperature. The integral of the measured curve gave a $\Delta H_p = 31.2$ kcal/mol, in good agreement with the earlier measurement.[9] The polymerization is exothermic with a long induction period, because of a dramatic "autocatalytic effect" observed in the polymer conversion vs. time curves. At about 10% conversion to polymer, the polymerization rate increases ~100-fold, which makes it possible to observe sharp exothermic DSC peaks in the polymerization of PTS. Due to this induction period the base line for the integral has to be adjusted until a fit of the data at low polymer conversion to previous extraction measurements is obtained. The adjusted ΔH_p value is ~36.5 kcal/mol (1.6 eV/ru). We also carried out various tests for heat loss, e.g., adding sapphire cover plates, without identifying any effects of poor heat collection on our results. We conclude that effectively all heat evolved in our modified apparatus is measured. This result is in contrast with the photoacoustic experiment[12] and represents a key advantage of the DSC technique.

III. Results

Table I
Summary of Photopolymerization Results for 4BCMU

weight, mg	ΔH_p,[a] kcal/mol	% polymer
1.15	22.04	5.6
1.82	21.42	4.4
2.12	22.45	3.0
3.11	21.48	3.1
3.38	21.77	3.0
4.20	21.66	2.2

[a] Average $\Delta H_p = 21.80 \pm 0.3$ kcal/mol.

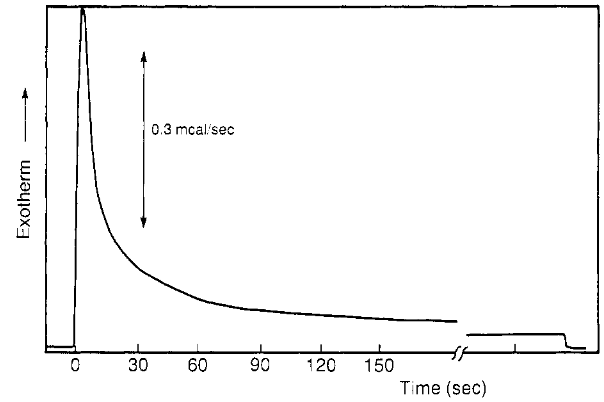

Figure 4. DSC signal for photopolymerization with increased light intensity. The polymerization rate is maximum at $t = 0$ and decays with time to a constant level for $t \to \infty$. A ratio $A(0)/A(\infty) = 25.2$ is obtained from the trace.

A typical DSC trace obtained for the photoinitiated polymerization of 4BCMU is shown in Figure 3. The point at $t = 0$ represents the opening of the light shutter and the onset of irradiation. The arrow marks the shutter closure (typically after 30 s), at which point the polymerization is terminated and the DSC signal returns to zero. The heat of polymerization measurements are carried out at light intensities too low to be calorimetrically detected when the light is focused on a radiation-resistant diacetylene or carbon black. Therefore, the area under the curve gives directly the heat of photopolymerization (in calories per gram of monomer). To obtain ΔH_p in kcal/mole the number of moles of polymer was determined spectroscopically as described in section II.

Table I lists the ΔH_p values derived from our photopolymerization experiments together with the sample weight and the conversion to polymer in percent. We obtain an average value of $\Delta H_p = 21.8 \pm 0.3$ kcal/mol (0.95 eV/ru). ΔH_p is independent of the sample weight up to about 6 mg. Above this weight we measured consistently lower values for ΔH_p, a result we attribute to heat loss problems due to poor heat transfer through the larger samples. The photoinitiated heat of polymerization is considerably lower than the ΔH_p value derived from the thermal polymerization studies of PTS ($\Delta H_p = 1.6$ eV/ru). We will discuss this result in the next section within the framework of the kinetic model for polymerization briefly described in the Introduction. We now turn to determination of the quantum yield, nq.

Following the kinetic model for photopolymerization of diacetylenes developed in ref 5 and used by Chance and Shand to interpret their photoacoustic results, the ratio $A(0)/A(\infty)$ of the heat evolved on irradiation at time $t = 0$ and $t = \infty$ can be used to calculate the quantum yield nq. This ratio is given by

$$A(0)/A(\infty) = 1 + nq\Delta H_p/h\nu \qquad (1)$$

if all heat is collected (or measured with equal effectiveness for monomer and polymer). Here, $h\nu$ is the photon energy and nq the number of polymer repeat units produced per absorbed photon. Implicit in this kinetic model is the assumption of linear light intensity dependence for the photopolymerization process, which we have confirmed. If I_0 is reduced by a factor of 3, the maximum of our DSC signal in Figures 3 and 4 is also reduced by a factor of 3 and the time scale for the reaction is extended by a factor of 3. Note that this linearity also shows that instrument response times do not affect our $A(0)/A(\infty)$ measurements in this intensity range.

In our experiment the heat evolved during polymerization was measured directly with the DSC apparatus. In order to measure the ratio $A(0)/A(\infty)$ the DSC signal was recorded on a HP 7047A X–Y recorder for a faster response and greater sensitivity than could be obtained with the Data Station. The incident light intensity I_0 was increased by using a 150-W Xe arc with a monochromator (254 nm, 20-nm band-pass). This experimental setup gave a measurable DSC signal after the polymerization was completed. This signal $A(t = \infty)$ is due to a complete absorption of light by the polymer and subsequent radiationless transitions leading to a heating of the sample detected by the DSC. (Poly(diacetylenes) do not fluoresce in their crystalline state; diacetylenes of the type investigated herein also do not fluoresce.)

Figure 4 shows such a DSC trace. The polymerization rate is maximum at $t = 0$. Therefore, the DSC signal has a maximum at the beginning and decays with time to a constant level for $t \rightarrow \infty$. The polymerization is practically complete after 2.5 h and the signal remains unchanged after 15 h of irradiation. A ratio $A(0)/A(\infty) = 25.2$ is deduced from the trace. The same ratio is obtained with a factor of 3 decrease in intensity. (With a factor of 3 increase the ratio decreases by about 15% due presumably to instrument response time limitations on the initial height.) Using our measured $\Delta H_p = 0.95$ eV/ru and a photon energy $h\nu = 4.88$ eV, we obtain a quantum yield $nq \simeq 125$ at 50 °C. We have also carried out measurements of the temperature dependence of the initial polymerization rate over the temperature range 30–65 °C. The temperature dependence is Arrhenius in nature and yields an activation energy of ca. 0.3 eV. Thus, the room-temperature (25 °C) quantum yield is predicted to be $nq \simeq 60$. This result is in good agreement with the value estimated by Prock et al.[13] from their photoacoustic experiments, $nq \sim 150$ (after correction with our ΔH_p value). Our results are also in good agreement with the quantum yield derived from absorption measurements of thin films,[16] where $nq \cong 70$ was estimated with an uncertainty of about a factor of 2, and with results of Bhattacharjee and Patel,[17] where a lower limit $nq > 50$ was estimated. We should also note in passing that if we assume that the propagation length for γ-ray polymerization (which has been measured as 2400 ru)[18] is the same for UV, we obtain an estimate of 0.025 for q at 25 °C.

IV. Discussion

The thermal polymerization process involves the vibrational excitation of the monomer ground state to the biradical dimer intermediate $R\dot{C}{=}C{=}C{=}C(R){-}(R)C{=}C{=}C{-}\dot{C}R$. The measured activation energy $E_a^{th} = 1$ eV is then roughly the difference in the energy between two diacetylene monomers and the biradical dimer. Further addition of monomer units to the dimer leads to the trimer, tetramer, etc., with the release of 1.6 eV per addition as derived from the thermal polymerization of PTS. This results in the reaction diagram of Figure 1. Simple thermochemical calculations show that these values are reasonable for thermally polymerizable diacetylenes.[9]

The same biradical dimer is thought to be the intermediate in the UV polymerization process. The 4BCMU monomer absorption spectrum shows a vibronic structure with a progression of 2300 cm^{-1}, consistent with the triple-bond stretching frequencies. It has been shown previously that polymerization occurs with excitation anywhere in the monomer absorption band. The photon energy used in our experiments (260 nm) is very close to the first absorption peak of the monomer (255 nm). Radiation creates excited singlet states, which can initiate chains, return to the ground state nonradiatively, or undergo intersystem crossing to form triplets, which could then initiate chains. It has not been established whether singlets or triplets are the primary chain initiation species. Since the photopolymerization rate is directly proportional to light intensity, the monomer excited state must then interact with the monomer ground state to form the biradical dimer.

If the biradical dimer is the intermediate in both the thermal polymerization and photopolymerization, then the energy released on addition of monomer units to the chain, ΔH_p, should be the same for both processes. Unfortunately, in our case 4BCMU is thermally inactive and a direct comparison is not possible. The relatively high activation energy we obtain for 4BCMU photopolymerization (0.3 eV compared to 0.1 eV for PTS)[5] indicates that there might be some energetic contribution from the chain propagation event to the overall activation energy.[19] This contribution is shown in our reaction diagram as a barrier for forming the trimer, tetramer, etc. Our measured $\Delta H_p = 0.95$ eV/ru suggests that the energies in the reaction diagram of Figure 1 should be moved up as indicated by the dashed curve. The dimer state would be closer in energy to the excited state, leading to a stronger nonradiative coupling between these two states, thus explaining why 4BCMU is a very photoreactive material. At the same time the difference in energy between the monomer ground state and the dimer would be greater than 1 eV, thus making 4BCMU a thermally unreactive material. Thus there is a satisfying internal consistency with the UV and thermal results. If this model is correct, a "compensation" effect is suggested wherein high photoreactivity suggests low thermal reactivity and high thermal reactivity suggests low photoreactivity. Though the 4BCMU and PTS results are adequately explained by this compensation effect, the extent of its applicability to other diacetylene compositions remains to be seen.

A remaining question involves the unexpectedly small ΔH_p for 4BCMU. There exist several possible explanations for the lower ΔH_p value. The photopolymerization process is inhomogeneous and conversion to polymer is incomplete. In that case, lattice strain energies could play a role. However, we do not believe that this effect could account for such a large difference in energy, since the strain energy depends on the difference between monomer and polymer lattice parameters, which we believe is very small by analogy to other compounds similar to 4BCMU.[20] A more likely explanation involves the intramolecular hydrogen bonds between the polymer substituent groups. It is well-known that the urethane-substituted diacetylenes show strong intramolecular hydrogen bonding between the C=O and N—H groups on adjacent substituents in solutions as well as in the solid state.[15] In solution, this hydrogen bonding controls the planarity of the backbone. In the case of 4BCMU, where four CH_2 groups link the side group to the backbone, molecular models demonstrate that a considerable distortion of the CH_2 groups and possibly the backbone is required for the formation of intramolecular hydrogen bonds. This idea is supported by the X-ray structure of the analogous polymer crystal poly-TCDU [$R = (CH_2)_4OCONHC_6H_5$], which clearly shows intramolecular hydrogen bonding and distortion in the $(CH_2)_4$ linkage.[21] No such distortion is required for urethane-substituted diacetylenes with three CH_2 groups like 3BCMU.[15,22]

Therefore, we suggest that the barrier to dimer formation (E_a) is increased and the heat released per propagation event, ΔH_p, is decreased due to the intramolecular hydrogen-bond network. We do not suggest that the hydrogen bonds are broken, but that they anchor the side groups so that usual side-group reorganization (in response to the monomer-to-polymer geometric transformation) are made difficult. Thus the side groups are distorted with strained bonds and, perhaps, the hydrogen-bond network is disrupted or substantially weakened. The energies involved should be about 0.4–0.7 eV/ru, which is in the range of the differences observed between thermal polymerization (1.6 eV/ru) and our photopolymerization (1.0 eV/ru) ΔH_p values. It is interesting to note that Desai et al.[14] obtain a very low value of 19 kcal/mol for the heat of polymerization of another diacetylene, *N*,*N*′-bis(2,4-dinitrophenyl)-2,4-hexadiyne-1,6-diamine (DNPNH). They attribute this to breaking of secondary hydrogen bonds on the DNPNH monomer sites during polymer formation. Based on available infrared data for our material, 4BCMU, we do not believe the hydrogen bonds are completely broken during reaction.

In summary, the energetics of 4BCMU polymerization are believed to be importantly influenced by an unfavorable side-group interaction in the polymer compared to that in the monomer. Our results could, therefore, suggest that a favorable polymer side-group interaction could lead to lower thermal activation energies and higher ΔH_p values.

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Registry No. 4BCMU, 68777-92-4.

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EPR Application to Polymers. 2. Spin Probing of Poly(phenylacetylene)

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ABSTRACT: Line shape changes in the electron paramagnetic spectrum of spin-probed poly(phenylacetylene) have been studied as a function of temperature. The line shapes have been simulated by using the stochastic Liouville theory of slow-motional effects on EPR spectra. Correlation times based on the moderate jump model have been calculated. It was found that the nitroxide spin probe exhibited anisotropic rotation whose anisotropy increased as temperature decreased. This has been interpreted as due to the intimate interaction between the nitroxide spin and the polymer chains which possess the π-delocalized electrons. The activation energy calculated from the temperature of rapid reorientation of the nitroxyl radical gives $E_\mathrm{a} = 8$ kcal mol^{-1}.

Introduction

There has been considerable interest in the synthesis[1–3] and physical properties[4–6] of polyacetylenes mainly because of the fact that these materials are highly polyconjugated and can have organic semiconducting properties useful in electronic technology.[7]

In the present article we extend[8] our investigations of poly(phenylacetylene) (PPA) using the spin-probing EPR technique. This method provides information about the molecular motions and dynamics by studying the line shape of the electron paramagnetic resonance spectra of spin probes embedded in polymer matrices. In contrast to spin-probe studies,[9] where the paramagnetic molecule is present as a "guest", free to move within the polymer matrix at concentrations of 10–100 ppm, the same species in the spin-label studies is immobilized by being chemically bound to the polymer chain.[10] The former technique is much simpler than the latter and it would be the method of choice as long as comparable information were obtainable.

Although many polymers have been spin probed, very few spectral simulation studies have been carried out to fully understand polymer chain motions and dynamics. In this work, we report the first study of the EPR spin probing of poly(phenylacetylene). We demonstrate how the theory of slow-tumbling EPR spectra of nitroxides can