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Nuclear Magnetic Resonance Study of Norbornene End-Capped Polyimides. 2. Solution and Solid-State Carbon-13 Study of 2NE/MDA and PMR Polymerization

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ABSTRACT: The thermally induced polymerization and cross-linking of two norbornene end-capped imide oligomers were studied by both solution and solid-state ^{13}C NMR. The results are compared to a simpler model compound, *N*-phenylnadimide. It is proposed that retro-Diels–Alder reaction and Diels–Alder reaction occur at the norbornene end-cap groups and that a three-dimensional polymer network is formed. The solid imide samples cured at various temperatures were studied at magnetic fields of 1.4, 3.5, and 7.0 T. Results were found to be consistent with the proposed mechanisms based on solution NMR studies.

Introduction

Polymers formed from norbornene end-capped imide oligomers have been shown to have good high-temperature properties.[1,2] We recently investigated the thermally induced polymerization of a simple norbornene end-capped imide compound by solution ^1H and ^{13}C NMR.[3] From that study, it was learned that most of its polymerization changes occurred at the location of the strained norbornene ring.

We report here a study of the thermal polymerization of two other norbornene end-capped imides and compare the results to those of the simpler model compound, *N*-phenylnadimide. The two imides were prepared from the reaction of the methyl ester of 5-norbornene-2,3-dicarboxylic acid (2 mol) with 4,4′-methylenebis[aniline] (1 mol) (2NE/MDA) (1) and from the reaction of the methyl ester of 5-norbornene-2,3-dicarboxylic acid (2 mol), 4,4′-methylenebis[aniline] (2 mol), and the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (1 mol) (2NE/2MDA/BTDE, or PMR for polymerization of monomeric reactants) (2). Unlike *N*-phenylnadimide (PN), which we recently studied,[3] both 2NE/MDA and PMR prepolymers are of higher molecular weight. Furthermore, these two prepolymers are end capped with strained norbornene rings at both ends, and, thus, when heated under pressure, they polymerize to form a three-dimensional network. To reach a full cure, a temperature of 315 °C for 1 h is generally required. We have found that 2NE/MDA cured above 275 °C and PMR cured above 250 °C for 1 h were totally insoluble in common NMR solvents. Even those samples cured under milder conditions were only partially soluble, leaving some undissolved particles suspended in the solution. In order to achieve a better understanding of the polymerization and cross-linking mechanisms as well as the final structures of these polyimides, we have employed both solution and solid-state NMR techniques to study the thermally induced polymerization of the above-mentioned two imides.

Previously, most high-resolution ^{13}C NMR studies have been limited to liquids; in solids the homo- and heterodipolar interactions give rise to line broadening on the order of 25 kHz, and further line broadening arises from the chemical shift anisotropy (CSA). The CSA broadening of an aromatic carbon in a 1.4-T field is on the order of 2 kHz and is approximately 5 kHz at 3.5 T. Since the demonstrations[4–6] that the combination of magic-angle sample spinning (MASS)[7,8] and dipolar decoupling with cross polarization[9] could yield high-resolution spectra in organic solids, considerable interest has developed to utilize this technique in the study of polymers. In our study of the polyimides, techniques of MASS, high-power decoupling, and cross polarization were used.

Experimental Section

2NE/MDA (1). The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE, 19.6 g, 0.1 mol) and 9.9 g (0.05 mol) of 4,4′-methylenebis[aniline] (MDA) were dissolved in 50 mL of dry methanol. The solution was refluxed, with stirring, for 2 h. It was then rotary evaporated to eliminate most of the methanol. The remaining viscous gel was oven dried at 150 °C for 2 h. The product is the fully imidized (determined from ^{13}C NMR) white prepolymer, mp 244–246 °C (dec).

PMR Prepolymer (2). The synthetic method as described by Serafini[1] was followed.

Polymers. Polymers were prepared following the procedure outlined in our previous paper on polyimides.[3] Since these higher molecular weight compounds do not flow as well as *N*-phenylnadimide when melted, curing rates of 10 °C/min from ambient to 250 °C and of 5 °C/min above 250 °C were used to minimize void formation.

Solution-State NMR Measurements. All solution NMR measurements were done on a Varian XL-100-15 spectrometer. Sweep width of 5000 Hz and 8K data points were generally used to give a 1.25-Hz resolution. The aromatic-olefinic region of the PMR prepolymer was further studied by using a 2-kHz sweep width and 8K data points to give a better resolution. A 60° pulse angle and 1.5–3-s cycle time were used in most cases. All samples were pulverized before they were dissolved in NMR solvents. The solutions were filtered to eliminate any undissolved materials. Me_2SO-d_6 and $CDCl_3$ were used as solvents for 2NE/MDA cured up to 275 °C and for PMR cured to 200 °C. Samples of PMR cured at 250 °C for 1 h were studied in Me_2SO-d_6. All samples utilizing $CDCl_3$ as solvent were studied at 30 °C and samples utilizing Me_2SO-d_6 as solvent were studied at both 30 and 80 °C.

Solid-State NMR Measurements. Single-contact cross polarization and MASS were used for all cases. Experiments were carried out on three separate spectrometers:

(1) A modified Bruker SXP pulsed NMR spectrometer was used with a ^{13}C Larmor frequency of 15 MHz. The protons were spin-locked at a field of 12.5 G, which also provided decoupling. The Hartmann–Hahn[10] condition was matched for 1.0 ms. The sample spinner was of modified Lowe geometry[7] and has a sample volume of 280 μL. Utilizing a recycle time of 2 s, 10–18K transients were used for each sample. Chemical shifts are relative to Me_4Si and the scale is based on ethylene glycol. Experimental temperature was 30 ± 2 °C. Samples were spun at 2.2 kHz.

(2) A Nicolet NT-150 NMR spectrometer with a modified double-tuned coil and spinning system was used. The protons were spin-locked in a field of 15 G or more, which also provided

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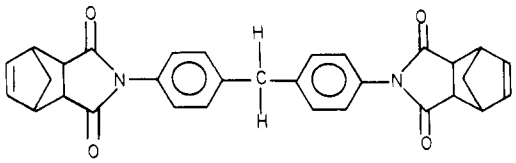
Chart I



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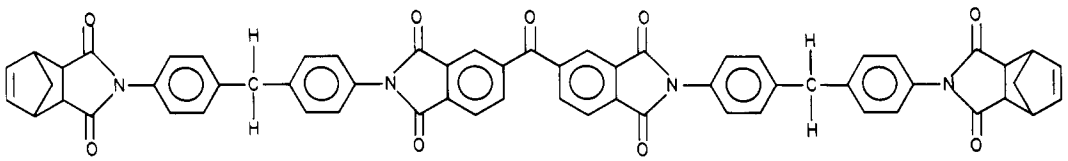

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Table I
^{13}C NMR Signals Observed in Addition to Those of the Endo-Cis Oligomers in the Curing of Three Polyimides[a]

	chemical shift												
PN <275 °C		176.9	138.1					47.9			45.9	43.0	
PN ≥275 °C	177.3			135.8	53.4	51.3	48.2		46.5				42.1 29.1
2NE/MDA <250 °C		177.0	138.0					47.8			45.8	43.0	
2NE/MDA ≥250 °C	177.5			135.7	53.4	51.1	48.0		46.3				41.9 29.1
PMR 200 °C			138.0					47.9			45.5	42.9	
PMR 250 °C[c]		(176.8)	(137.8)	135.7		50.5	48.1	(47.5)	47.0	45.8	(45.1)	(42.6)	*b*

[a] All samples studied in $CDCl_3$ unless otherwise indicated. Chemical shifts are given in ppm from Me_4Si. New aromatic signals are not included. [b] No conclusions were made due to solvent signal interference. [c] PMR cured at 250 °C was studied in Me_2SO-d_6 due to its insolubility in $CDCl_3$. Chemical shifts in parentheses are signals observable at 200 °C curing temperature.

decoupling. The Hartmann–Hahn condition was matched for 1.5 ms for 2NE/MDA and 1.0 ms for PMR samples. Samples were spun at 1.6–2.0 kHz. The Kel-F spinner was of Andrew geometry[8,11] and has a sample volume of 360 μL. The number of data points was 1000 and ±5000-Hz sweep width (quadrature detection) was used. The number of transients for all 2NE/MDA samples was 1000. A total of 4000 transients was used for each PMR sample. Chemical shifts are relative to Me_4Si and the scale is based on the results of the solution spectra. Pulse recycle time was 1.5 s and experimental temperature was 40 °C.

(3) A commercial Bruker CXP-300 spectrometer was used. The ^1H 90° pulse was 4 μs and the cross polarization time was 3 ms. Sample volume was ~300 μL and had a MASS speed of ~4 kHz. A sweep width of 50 kHz and 4K data points were used. Utilizing a recycling time of 4 s, 200 transients were used for uncured 2NE/MDA and the experimental temperature was kept at ~30 °C.

The following samples with specified curing temperature and time were run on the above-mentioned spectrometers. All samples were ground and used in a powder form. Bruker SXP: 2NE/MDA, uncured, 232 °C (1 h), 288 °C (1 h), 315 °C (2 h). Nicolet NT-150: 2NE/MDA, uncured, 232 °C (1 h), 288 °C (1 h), 315 °C (2 h); PMR, uncured, 275 °C (1 h), 315 °C (2 h). Bruker CXP-300: 2NE/MDA, uncured.

Results and Discussion

Figure 1 shows the solution NMR spectra of 2NE/MDA cured at various temperatures. Results similar to those for *N*-phenylnadimide are observed here. At a curing temperature of 200 °C, four new resonance signals appear at 138.1, 48.0, 45.9, and 43.0 ppm. A carbonyl signal at 177.0 ppm is not observed in the figure due to the short pulse delay time but it can easily be seen under different experimental conditions or in samples cured at higher temperatures. These five signals, after quantitative, off-resonance, and empirical calculations, are determined to be due to the endo–exo isomerization of the nadic end-capped groups. Higher curing temperature increases the amount of exo isomers and the formation of new compounds. Figures 1C and 1D show the spectra of 2NE/MDA cured at 250 and 275 °C. The new resonances are indicated by arrows and their chemical shifts are listed in Table I.

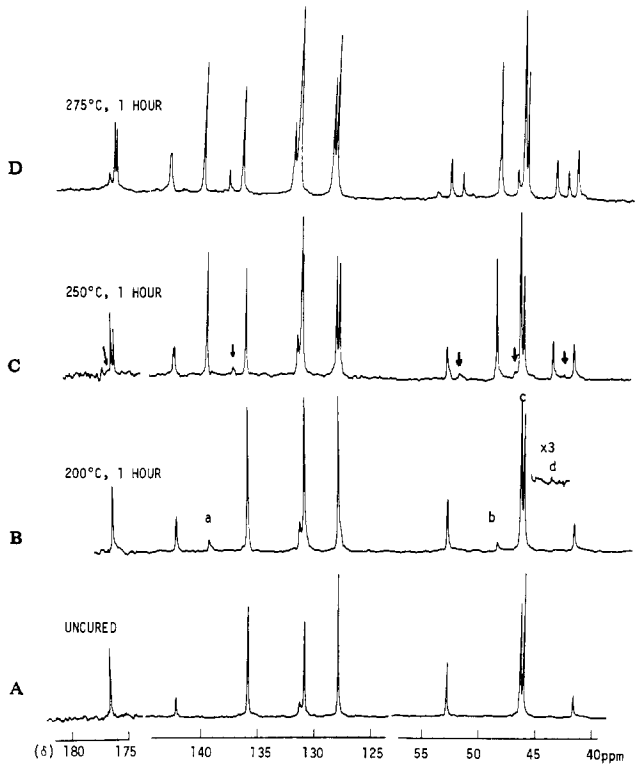

Figure 1. ^{13}C NMR spectra of 2NE/MDA in $CDCl_3$. The vertical scale of the three regions has been adjusted to facilitate comparison. Peak c is not resolved in this magnetic field (2.3 T) but can be resolved by using either a higher field or Me_2SO-d_6 as solvent.[3]

For PMR resin cured at 200 °C, five new ^{13}C resonance signals corresponding to PN and 2NE/MDA exo isomers are again observed (Table I). The results in Table I suggest that at lower curing temperatures, both PMR and 2NE/

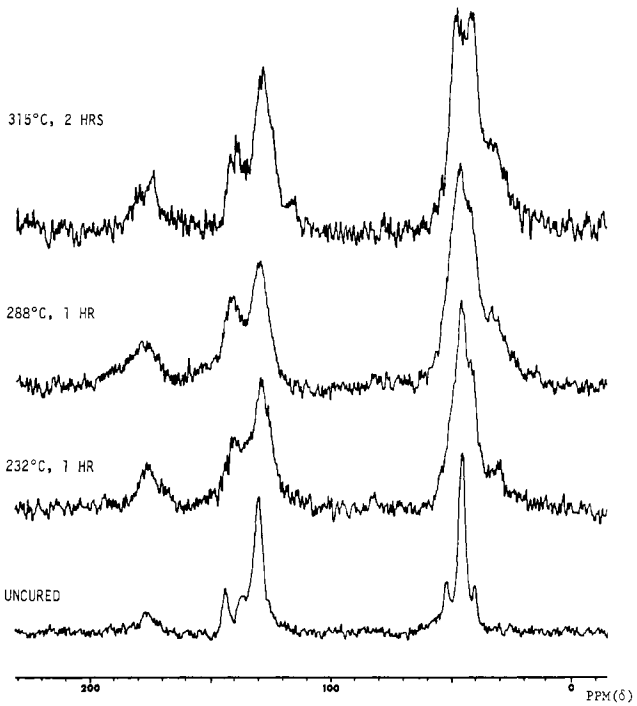

Figure 2. Solid-state ^{13}C NMR spectra of 2NE/MDA at 1.4 T. The 110–120-ppm signal of the 315 °C sample may be an artifact.

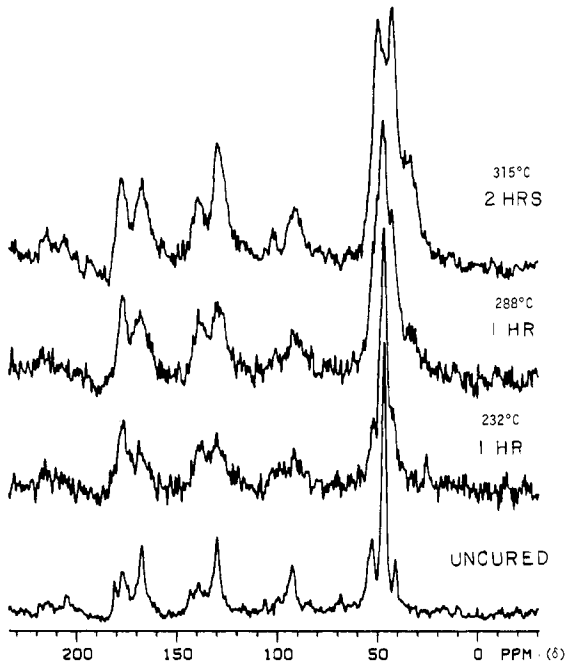

Figure 3. Solid-state ^{13}C NMR spectra of 2NE/MDA at 3.5 T.

MDA react similarly to PN, i.e., undergo an endo–exo isomerization. The data also suggest that even at higher curing temperatures, 2NE/MDA, a di-end-capped imide oligomer, may also react via a Diels–Alder reaction, similar to *N*-phenylnadimide. However, since the di-end-capped polyimides cured at higher temperatures only dissolve partially in the NMR solvents, a conclusion based purely on the solution NMR results may merely reveal the mechanisms of those molecules that are in solution. A solid-state NMR study of the di-end-capped imides cured at various stages is necessary to support our conclusion.

Figure 2 shows the ^{13}C solid-state NMR spectra in a magnetic field of 1.4 T of 2NE/MDA cured at various temperatures. The 2.2-kHz spinning speed is sufficient in this field to eliminate all spinning sidebands from the chemical shift anisotropy. The uncured oligomer has a line width on the order of ~75 Hz, which is probably due to the spread of the isotropic chemical shifts of the highly amorphous compound. As the polymerization and cross-linking progress, the line width observed broadens, which is expected with decreasing order in the polymeric system.

Although the completeness of cross polarization may not be the same among the carbonyl, olefinic, and aliphatic groups, a qualitative comparison within each figure should still be informative. In order to make sure the spectral changes observed are actually due to curing rather than due to the change in the cross-relaxation rate, brief experiments with cross-polarization time varying from 500 μs to 5 ms were performed on the uncured 2NE/MDA.

Results consistent with those observed in the solution NMR are observed here. Comparing the sample cured at 232 °C with the uncured one, it is evident that resonance signals appear at 177, 138, 48, 46, and 43 ppm in the 232 °C sample. These five resonance signals have been observed in the curing of the soluble *N*-phenylnadimide and are proposed to arise from an endo–exo isomerization reaction of the nadic group.[3] In addition, a broad signal at 30–40 ppm is observed for the 232 °C sample. Unlike the five resonances just mentioned, this signal is not observed in the solution spectrum of the same material. In the soluble *N*-phenylnadimide, the signal is observed only after a much higher curing temperature (285 °C for 1 h) and is probably due to polymer structures and the products of the Diels–Alder reaction. Other major resonance signals in soluble samples believed to be related to Diels–Alder reaction are seen at 135.7, 51.1, and 41.9 ppm.[3] Of these resonances, the presence of the olefinic peak (135.7 ppm) can be seen rather clearly in the solid-state spectrum of the 232 °C sample, while the presence of the other two is not so obvious because they overlap with other newly emerged resonance signals (48, 46, and 43 ppm). The observation of signals at 135.7, 51.8, 41.9, and 30–40 ppm for 2NE/MDA after 232 °C curing suggests that the polymerization reaction may possibly occur at a much lower curing temperature (232 °C) in 2NE/MDA than that in soluble cured *N*-phenylnadimide (observation of retro-Diels–Alder products at 250–275 °C and polymerization at 285 °C).

In studying the spectrum of the solid sample cured at 288 °C, one can clearly see that the new resonance signals observed in the 232 °C sample have increased in intensity. Most noticeable are signals at 138, 51.8, 47.8, 43, and 41.9 ppm. In addition, broadening of the carbonyl signals at lower field is also observed. Although this new resonance signal cannot be resolved due to the broad line width present, it can be attributed partly to the new carbonyl peak at 177.5 ppm, based on the solution NMR study of the 275 °C sample. Also clearly observed in the spectrum is the decreased intensity of the olefinic peak (134.9 ppm) of the uncured prepolymer, which is to be expected as the polymer norbornene end caps become part of the backbone of the new polymeric product. Judging from this spectrum, the products of both Diels–Alder reactions and polymerization are present in the 288 °C cured sample, and some of the unreacted prepolymer is present as well. Although some spectral difference is observed between samples cured at 315 °C (2 h) and at 288 °C, it is difficult to determine whether the starting reactants have totally polymerized based on Figure 2. In order to achieve further understanding of the polymerization mechanisms and polymer structure of the polymers cured above 288 °C, we studied the four 2NE/MDA samples in a 3.5-T magnetic field. Their spectra are shown in Figure 3. Since the CSA

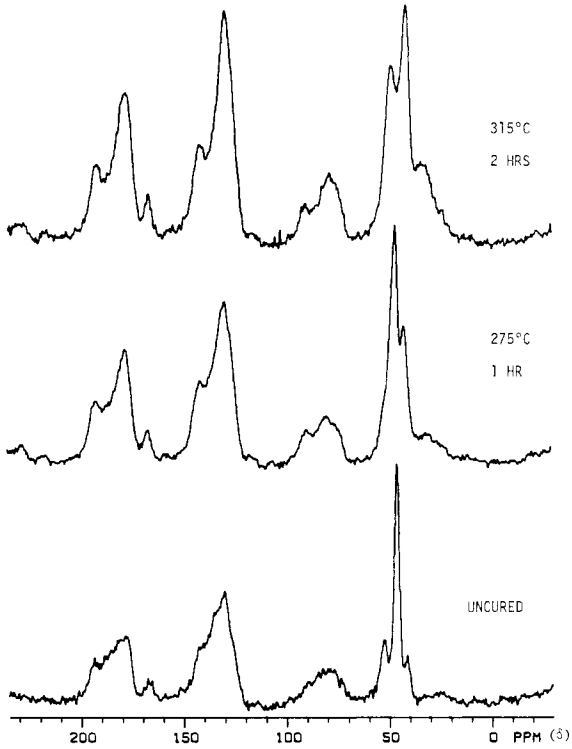

Figure 4. Solid-state ^{13}C NMR spectra of PMR at 3.5 T.

broadening is a function of the magnetic field, increasing H_0 increases the spinning speed requirement for disappearance of sidebands. These sidebands can be removed only when $\nu_{rot} \geq |\sigma_1 - \sigma_2|$, where ν_{rot} is the MASS speed and the σ's are the minimum and maximum chemical shift principal values of the nuclei concerned. For the carbonyl and aromatic-olefinic groups the 1.6–2.0-kHz spinning speed in this static field is not sufficient to remove the spinning side bands from the chemical shift anisotropy. Although several approaches of sideband elimination have been reported,[5,12,13] some technical difficulties and the very broad line widths due to the dispersion of isotropic chemical shifts we encountered made the application of these methods rather difficult. Consequently, spinning sidebands whose relative amplitude depends on the anisotropy in the chemical shift tensors[5] are observed for both the aromatic-olefinic and carbonyl groups. Fortunately, there are no sidebands due to the aliphatics, and sidebands due to other functional groups do not cause interpretive problems to the aliphatics. Thus, information can still be derived by studying the aliphatic resonances and the upper (higher field) sideband of the aromatic-olefinic groups.

The spectral results obtained on the 3.5-T spectrometer are essentially the same as observed at 1.4 T. In spite of a 2.5 order-of-magnitude increase in the static field, no significant improvement in resolution is observed. This is probably due mainly to the dispersion of the isotropic chemical shifts contributed from the amorphous nature of the samples. Other line-broadening factors, e.g., misadjustment of the magic angle and off-resonance proton irradiation,[14,15] also become more significant here than in the lower static field. However, the upper sideband of the olefinic-aromatic groups of the 315 °C sample clearly shows the disappearance of the prepolymer olefinic group. This indicates that all of the prepolymer has polymerized at this curing temperature. For the uncured 2NE/MDA samples, studies in a 7-T magnetic field were done in addition to the 1.4-T and 3.5-T fields. Again, no significant improvement in resolution was observed. However, compared with spectra taken on the 1.4-T instrument, spectra obtained at 3.5 and 7 T showed signficant improvement in sensitivity, as predicted by theory.

Scheme I

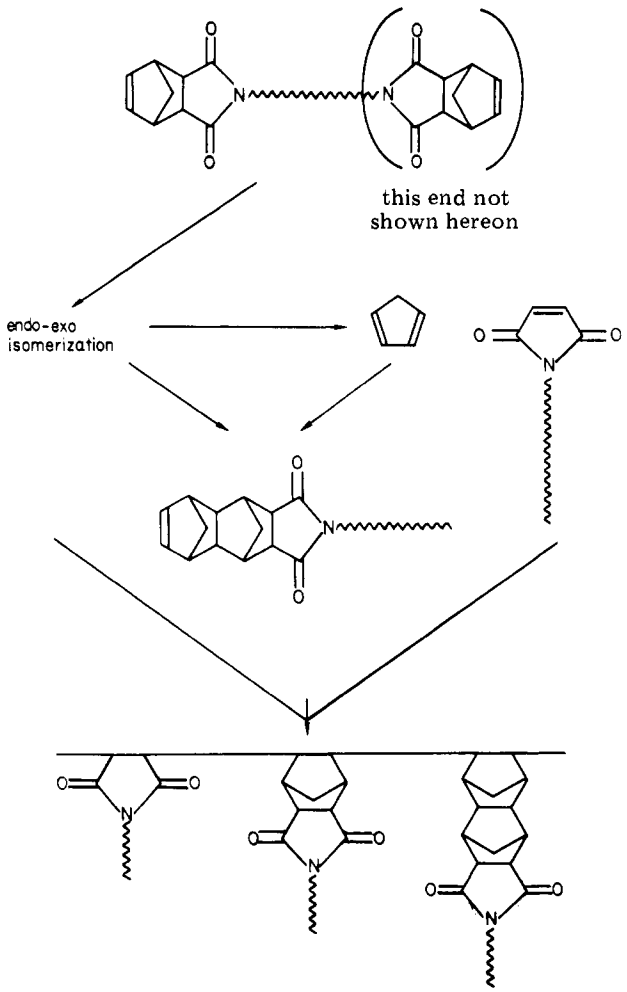

Figure 4 shows the spectra of PMR in a 3.5-T field with a sample spinning speed of approximately 2 kHz. From the results of solution NMR study it has been found that for samples cured at 200 °C at least five resonance signals exist which are related to the endo–exo isomerization of the nadic end-cap group (Table I). The spectrum of the 275 °C cured solid sample clearly shows the presence of a broad signal at 30–40 ppm in addition to the above-mentioned five peaks. In order to make sure this peak was not due to the second upper sideband (at 20–25 ppm in Figure 4) of the aromatic-olefinic group, we also studied all solid PMR samples at two different spinning speeds, which eliminates the possibility of misassignment. Although the first upper sidebands of two of the carbonyls overlap with the resonance signals of the olefinic-aromatic group, the appearance of the new olefinic signals can be seen by studying the first upper sideband of the olefinic-aromatic group. It is possible that the second upper sideband from the carbonyl group is overlapped with it but the intensity from the carbonyl sidebands will be very weak and its contribution can be practically ignored. In the 315 °C cured solid sample, the decreased intensity at 46 ppm and the fast-growing signals at 41–42 and 30–40 ppm suggest the disappearance of the prepolymer as well as the domination of the polymerization product.

The above results suggest that the mechanisms observed in the solution NMR studies are also operative in the more highly cured polyimides, i.e., endo–exo isomerization and retro-Diels–Alder reaction at lower curing temperature and

the consequent Diels-Alder reaction of the cyclopentadiene with the more stable nadic group. At higher temperature, all these groups polymerize at basically the olefinic positions, forming a three-dimensional cross-linked polymer network (Scheme I).

Conclusion

The results of the solution and solid-state ^{13}C NMR study of the 2NE/MDA and PMR imides indicated that the polymerization mechanisms of these more complex imides are consistent with those found in the simpler, soluble imides, i.e., retro-Diels-Alder reaction of the end-capped nadic group and further Diels-Alder reaction of the oligomers and cyclopentadiene to form the various isomeric end-capped groups. These groups then polymerize through reaction of the nadic olefinic group to form the three-dimensional polymer network. This conclusion is derived from the mutually complementary data of solution and solid-state ^{13}C NMR and after comparison with the data of the polymerization of the simpler, single end-capped imide model compounds.

Solid-state ^{13}C NMR can be used to study the curing of polymers which are insoluble or only sparingly soluble in common NMR solvents. This can be especially effective if complementary solution NMR data are utilized in the study. High ^{1}H decoupling field, cross polarization, and MASS are essential in order to obtain reasonably high resolution ^{13}C NMR spectra of these amorphous solid polymers. It appears that little or no improvement in resolution of these amorphous polymers is observed with increasing static field in many cases; however, the expected increase in sensitivity is clearly observed.

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Dynamics of Dilute Polymer Solutions

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ABSTRACT: Polystyrene, poly(tetrahydrofuran), and poly(dimethylsiloxane) in dilute solution in C_6D_6 and in CS_2 have been observed by the neutron spin-echo technique. Motion over distances up to 30 Å has been measured with an energy resolution of 0.01 μeV ($\sim 10^7$ Hz). Systematic deviations from Q^3 behavior at higher frequencies have been fitted to theoretical predictions and characteristic length and frequency parameters extracted for each polymer.

1. Introduction

A linear polymer molecule in dilute solution adopts a random-coil configuration which is continuously changing as rotation about backbone bonds occurs. The driving force for this Brownian motion is the thermal energy and its rapidity depends both on the energy barriers to internal rotation of the bonds and on the viscous drag of the solvent.[1] The motion may be observed directly in scattering experiments where probe particles (neutrons or photons) exchange energy with the polymer molecules. Alternatively, the molecular motion of the polymer dominates the response of the solution to external applied forces, giving rise to the various moduli and the dynamic viscosity. The observation is strongly dependent on the frequency of the applied stress or the energy range covered by the scattering experiments. Brownian motion of the whole polymer molecule dominates scattering experiments at low energies, and only the overall molecular dimensions (e.g., the end-to-end distance $\langle r^2 \rangle$) and the solvent viscosity are important. At very high frequencies there is not time for cooperative bond rotations and the molecular response to stimulus is confined to local bending and stretching of the bonds. This motion is therefore highly dependent on the local chemistry of the polymer. Between these two extremes there lies a frequency range where measurement is sensitive to detailed changes in the coil conformation. Points on the chain not too far removed from each other have time to change their relative positions during the

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