Characterization of Bifunctional Interpenetrating Polymer Networks via Solid-State ^{13}C NMR Spectroscopy

Darrell W. Crick and Spiro D. Alexandratos*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

Received June 22, 1992; Revised Manuscript Received March 24, 1993

ABSTRACT: Bifunctional interpenetrating polymer networks (IPNs) have been synthesized and characterized via ^{13}C CP/MAS and DP/MAS NMR spectroscopy. The IPNs consist of polystyrene (PS)/poly(4-vinylpyridine), PS/poly(*N*-vinylimidazole), PS/poly(ethyl acrylate), PS/poly(4-vinylpyridine-*co*-ethyl acrylate), and PS/poly(*N*-vinylimidazole-*co*-ethyl acrylate). Both monomers of the second network are readily sorbed into the polystyrene support and result in well-defined networks. CP/MAS is used to identify the second network which, due to its relatively high rigidity, is transparent to DP/MAS. The acrylate-containing IPNs are subjected to a subsequent reaction, and the resulting polymers are characterized. CP/MAS is able to show that base hydrolysis leads only to ester cleavage without degradation of the networks and that all sites are accessible to the reaction.

Introduction

Interpenetrating polymer networks (IPNs) are a unique class of polymers in which one network is synthesized in the presence of another to yield a material consisting of two entangled, noncovalently bound networks. One subclass of these polymers is the sequential IPNs which are prepared by swelling one preformed network with a monomer solution and then polymerizing *in situ*.[1] IPNs have been the subject of extensive research and thoroughly reviewed.[1-5]

Bifunctional polymers are systems in which two different types of ligands are immobilized on a support and can cooperate synergistically to yield a reagent with enhanced complexing abilities relative to the monofunctional polymers. As applied to metal ion coordination chemistry, bifunctional polymers have been synthesized with ligands capable of ion exchange, bringing ions near a second type of ligand which interacts selectively with a targeted substrate. Selectivity has been achieved through reduction, coordination, and precipitation of targeted metal ions.[6] IPNs are now being studied as an alternative to the covalent immobilization of ligands onto a support for the preparation of well-defined bifunctional polymers.

In order to examine bifunctionality in IPNs, research described in this paper has focused on the development of solid-state NMR spectroscopy as a technique for identifying the functional groups present and their accessibility to reactants in subsequent chemical transformations. The accessibility of hydroxide ions in a hydrolysis reaction is detailed. Amidation and transesterification reactions will be the subject of a separate publication. The extent to which the reactions have gone to completion and whether side reactions, such as network degradation, have occurred are also examined spectroscopically.

Solid-state ^{13}C CP/MAS NMR has proven to be a powerful technique for the study of cross-linked polymers.[7,8] CP/MAS NMR spectra of such polymers, however, display broad line widths due to the presence of chemical shift anisotropy and dipolar coupling.[9] Ford et al.[10,11] have attempted to alleviate this problem by acquiring spectra of solvent-swollen gels; true solution-state behavior is not observed in these systems, though, due to restriction of the end-over-end motion caused by the cross-links.[9] As proposed by Doskocilova et al.,[12,13] and elegantly utilized by Frechet to characterize functionalized polystyrene gels,[9,14] residual solid-state behavior may be reduced by spinning the solvent-swollen polymer at the magic angle. Since the segmental motions present in the solvent-swollen sample cause the dipolar interactions necessary for cross-polarization to average to zero, DP/MAS NMR spectroscopy was utilized to acquire the polystyrene spectra.

The use of solid-state NMR spectroscopy to characterize IPNs is not as widespread as the use of thermal, mechanical, and electron imaging techniques. Nonetheless, ^{13}C line widths in polystyrene-containing IPNs have been studied in order to determine the degree of interaction between two networks, the microphase structure of the IPN, and structure–property relationships.[15,16] The research described in this paper presents a DP/MAS–CP/MAS study of the formation and subsequent chemical transformation of a series of sequential IPNs designed for use as ion-complexing agents. The domain size of the IPNs described below is expected to be extremely small due to their level of cross-linking: much more lightly cross-linked networks with more flexible cross-link agents show domain sizes of 150 Å; the domain size decreases with increasing cross-link level.[17]

Experimental Section

The synthesis of the sequential IPNs used for this study has been introduced.[18] Briefly, polystyrene xerogel beads cross-linked with 2% divinylbenzene (DVB) are swollen in a toluene solution of the appropriate monomers. The second network is formed by suspending the swollen beads in an aqueous phase containing stabilizers followed by polymerization at 80 °C for 12 h. Uncross-linked polymer is removed by Soxhlet extraction with methanol. The IPNs have 10% DVB in the second network. The IPNs synthesized within polystyrene (PS) as network I, along with their capacities as measured titrimetrically and by elemental analysis (mequiv/g (dry wt)), are PS/poly(4-vinylpyridine) (6.99), PS/poly(*N*-vinylimidazole) (4.38), PS/poly(ethyl acrylate) (4.56), PS/poly(4-vinylpyridine-*co*-ethyl acrylate) (2.24, 2.34), and PS/poly(*N*-vinylimidazole-*co*-ethyl acrylate) (2.62, 2.07). The three acrylate-containing IPNs were then refluxed with 2 M KOH in aqueous dioxane for 72 h. The base/acid capacities for the IPNs in the order given above are −/5.23, 3.25/2.50, and 3.33/2.55 mequiv/g, respectively.

All ^{13}C spectra were recorded on a Nicolet NT-200 spectrometer operating at 50.31 MHz for ^{13}C and 200.07 MHz for ^{1}H. A Doty Scientific standard 5-mm VT-MAS probe was used in conjunction with sapphire rotors and either vespel (CP/MAS) or double Viton O-ring sealed Macor end caps (DP/MAS). Samples for DP/MAS spectra were swollen in the appropriate solvent and packed into the rotor (75% full) without crushing. Samples for CP/MAS spectra were finely ground, and the rotors were fully packed. The data size was 8K zero-filled to 32K for CP/MAS and 16K

0024-9297/93/2226-3267$04.00/0

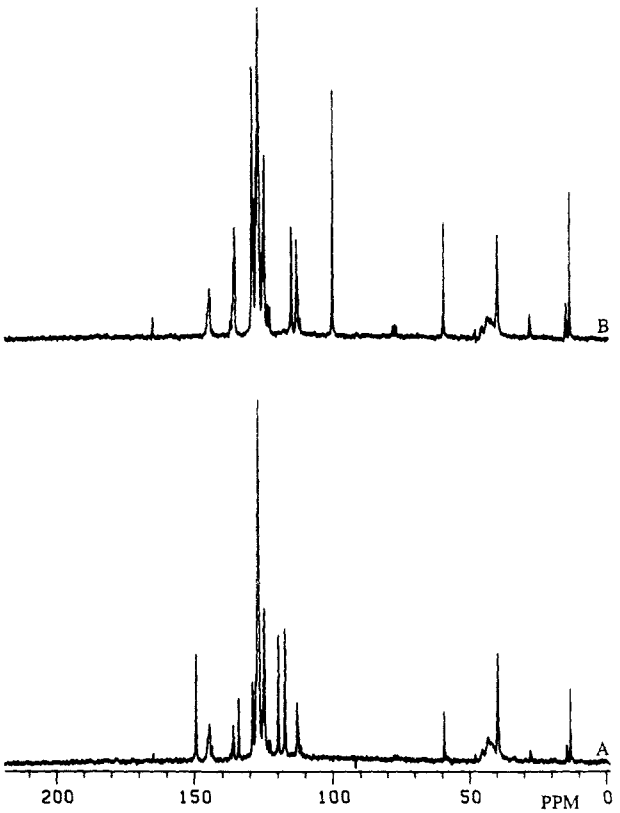

Figure 1. DP/MAS spectra of 2% DVB xerogel polystyrene swollen in $CDCl_3$ solutions of (A) VP/EA/DVB and (B) VI/EA/DVB.

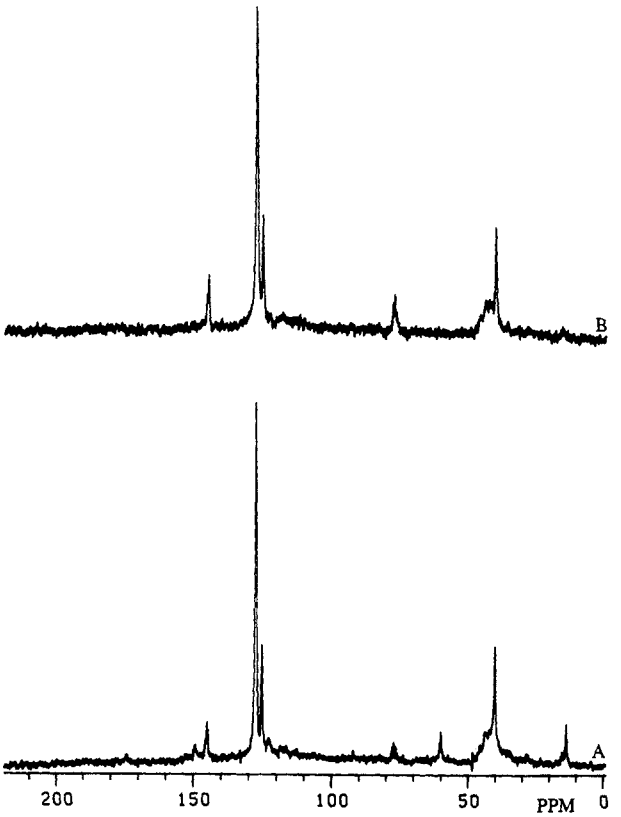

Figure 2. DP/MAS spectra of PS/VP–EA IPN swollen in $CDCl_3$ (A) before and (B) after reaction with 2 M KOH in aqueous dioxane.

zero-filled to 32K for DP/MAS spectra. All spectra were recorded at ambient temperature with a sweep width of ±15 kHz and spin speeds of 3.0–3.5 kHz. DP/MAS spectra were recorded with a pulse width of 2.5 μs (62°), a relaxation delay of 0.3 s, and 6000 scans. CP/MAS spectra were recorded utilizing an initial ^1H 90° pulse of 5.00 μs followed by a 1.00-ms cross-polarization contact time, a 10-s relaxation delay, and 500 scans. Exponential line broadenings of 5 Hz were used for DP/MAS and 30 Hz for CP/MAS spectra. The decoupling level was 5 W during DP/MAS signal acquisition, which is considerably lower than the 21-22 W used for the CP/MAS spectra. Chemical shifts are referenced to internal $CDCl_3$ (DP/MAS) and external hexamethylbenzene (CP/MAS).[19] Spectral subtractions were done with the software package provided by Nicolet. Spinning side bands were identified by recording a second set of spectra at a lower spin rate (2.0–2.5 kHz).

Results and Discussion

Figure 1 presents the DP/MAS spectra of 2% DVB xerogel polystyrene swollen in $CDCl_3$ solutions of 4-vinylpyridine (VP)/ethyl acrylate (EA)/DVB and *N*-vinylimidazole (VI)/EA/DVB. In addition to the polystyrene signals at 145, 128, 126, and 46–41 ppm, spectrum 1A shows the olefinic signals arising from DVB (113 ppm) and VP (117 and 120 ppm). The EA olefinic signals cannot be unambiguously assigned due to overlap with the DVB signal at 129 ppm. The carbons of the ethyl group, however, are visible at 59 and 13 ppm. Other features include the signal from the ester carbonyl at 165 ppm and the quaternary carbon of VP at 149 ppm. All peak assignments were made by comparison with ^{13}C spectra of the monomers in $CDCl_3$. The DVB contributes numerous lines to the aromatic region. Spectrum 1B shows the olefinic DVB peak at 113 ppm and additional peaks at 100 and 115 ppm from the VI. The EA resonances seen in spectrum 1A are also visible as is C-2 of the VI ring at 135 ppm. The small peaks at 28 and 14 ppm arise from the alkyl group of ethylvinylbenzene, which is the principal impurity in technical grade DVB.

Upon sequential IPN formation, the DP/MAS spectra of the IPNs swollen in $CDCl_3$ show only the polystyrene network clearly. At best, weak signals from some of the carbons present in the other network may be seen. Figure 2 shows the PS/VP–EA IPN before and after reflux with hydroxide. Before reaction, small ester resonances are seen at 60 and 14 ppm as well as small peaks from the VP aromatic carbons at 149 and 123 ppm. The small feature at 174 ppm may be due to the carbonyl of the ester group, but its signal-to-noise ratio is too small to permit unambiguous assignment. After reaction, no signals other than those from polystyrene are visible even though titrimetry shows the presence of a second network.[18] Similarly, the DP/MAS spectrum of PS/VI–EA shows only weak resonances in addition to the polystyrene signals. The absence of signals from the second network is explained by the fact that polystyrene (network I) is cross-linked with only 2% DVB while network II has 10% DVB. This 5-fold increase in cross-link level significantly decreases segmental motion in network II relative to that in network I and leads to greater solid-state behavior. Two factors may be operative. First, the decreased molecular motion will cause an increase in the observable chemical shift anisotropy and dipolar coupling which will be manifested as broadened lines. Second, the lack of rapid motion will dramatically decrease the relaxation rate. Since the relaxation delay used during the acquisition of the DP/MAS spectra was unusually short, it is probable that many of the resonances were saturated. Increasing the relaxation delay from 0.3 to 20 s, however, had little effect on the spectra. The use of H_2O as a swelling solvent with the VP–acid IPN did not enhance the signals from network II, but it did broaden the signals from the polystyrene network, presumably due to lack of good polymer/solvent interactions. Unfortunately, the choice of swelling solvent is extremely limited since it is necessary that the solvent

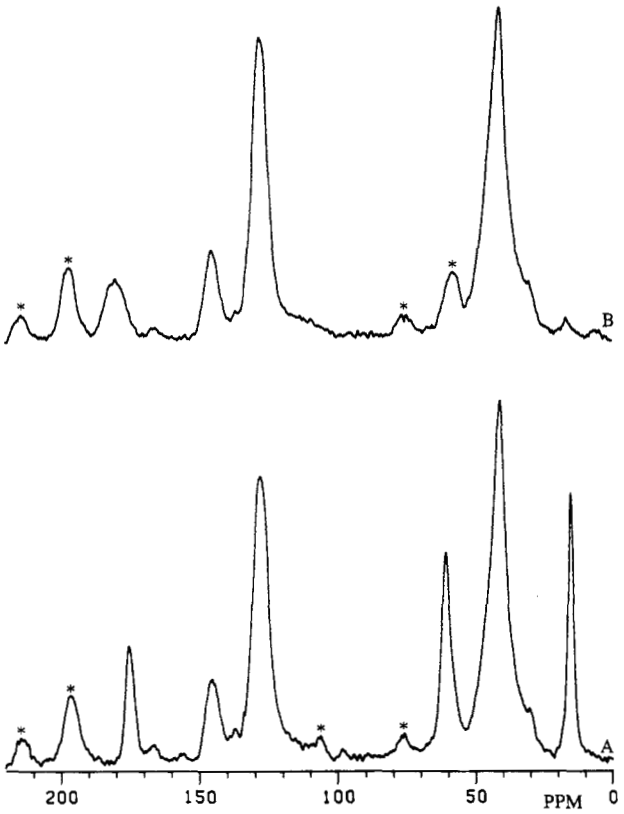

Figure 3. CP/MAS spectra of PS/EA IPN (A) before and (B) after reaction. Spinning side bands are indicated by asterisks.

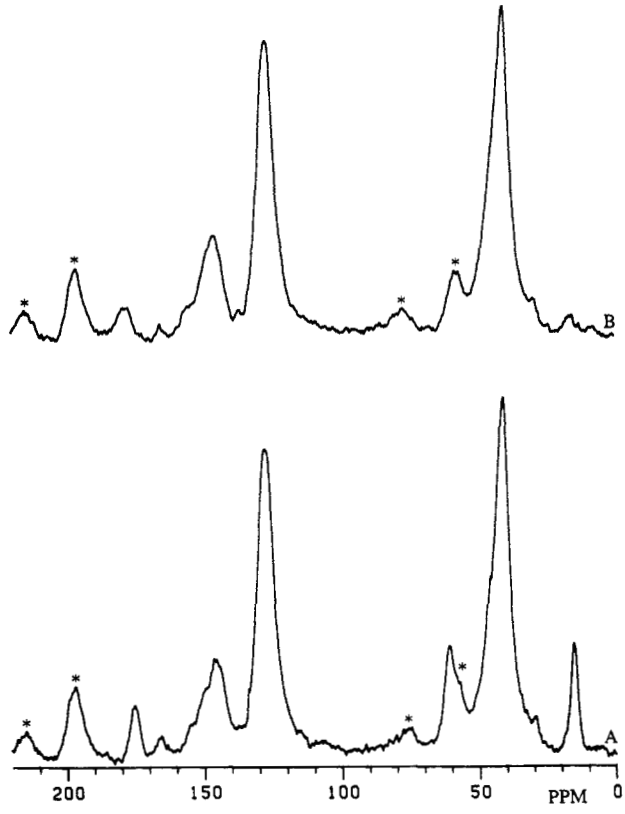

Figure 4. CP/MAS spectra of (A) PS/VP–EA and (B) PS/VP–acid IPNs.

be compatible with the Viton O-rings used to seal the rotor. Acetone, dioxane, and DMSO were found to damage the O-rings.

Since the rigidity of network II in an IPN can render it transparent to DP/MAS, its presence and proof of structure was attempted with CP/MAS. Standard CP/MAS parameters were used to acquire a complete set of spectra using finely ground IPNs packed dry into the rotor.

The CP/MAS spectrum of polystyrene is very similar to the DP/MAS spectrum though the line widths of all resonances are significantly larger in the former. Upon incorporation of a second network, the spectrum becomes more complex. Figure 3 shows the spectra of the PS/EA IPN before and after reaction with hydroxide. Whereas the DP/MAS spectrum shows only polystyrene peaks, the CP/MAS spectrum displays peaks at 175, 61, and 15 ppm in addition to those arising from polystyrene. These peaks are identifiable as the carbonyl and ethyl carbons of the ester by comparison with the linear poly(ethyl acrylate) spectrum.[20] After the IPN is refluxed in a basic solution, the ethyl resonances disappear and a broadened carbonyl peak shifts downfield to approximately 180 ppm, which is consistent with the spectrum of linear poly(acrylic acid).[21,22]

It has been reported that treatment with KOH can convert pyridine and 1-substituted imidazoles into 2-pyridinone and 1-substituted imidazolinones, respectively.[23,24] In addition, treatment with base can cause cleavage of the pyridine ring, leading to poorly characterized, colored compounds,[25,26] and can cleave substituted imidazoles to form alkyl-substituted formamides.[27] In the present study, the NMR spectra confirm that, in spite of the high concentration of KOH, the length of reaction, and the fact that the IPNs darken during hydrolysis, the measured capacities are due to undegraded ligands.

The spectrum of the PS/VP IPN is similar to that of polystyrene with the addition of two unresolved peaks at approximately 150 and 154 ppm. These are identified as aromatic VP carbons (C-2 and C-4) by comparison with the linear poly(4-vinylpyridine) spectrum.[28] Figure 4 shows the spectrum of PS/VP–EA before and after reflux with base. The parent sample shows both VP and EA features described above for the monofunctional IPNs. Hydrolysis is the sole reaction after reflux as indicated by a broadening and downfield shift of the carbonyl peak and disappearance of the ethyl peaks. The styrene and pyridine features remain unchanged.

The imidazole networks, in addition to the polystyrene signals, display a peak shoulder at 119 ppm and enhancement of the peak at 137 ppm which, though not well-resolved, are probably due to the VI aromatic carbons. A suspected VI backbone resonance appears at 52 ppm. Definite assignment of these peaks is made by comparison with the spectrum of the linear polymer[29] and by subtraction of the polystyrene spectrum from that of the PS/VI IPN (Figure 5). Although the subtraction does not leave a clean spectrum, it is clear that the peaks at 137 (ring C-2), 123–119 (ring C-4), and 54–52 ppm (backbone α-C) are due to the poly(*N*-vinylimidazole). The PS/VI–EA and PS/VI–acid IPNs (Figure 6) give spectra which display the same pattern found with VP IPNs. No peaks arising from heterocycle degradation products are observed. In particular, peaks associated with conversion of C-2 in both pyridine and imidazole (163 and 152 ppm, respectively)[30,31] are absent.

Conclusions

The chemical composition of sequential IPNs has been studied with solid-state ^{13}C NMR spectroscopy. Network differences in the cross-link level and swelling characteristics allow DP/MAS and CP/MAS to be used as complementary techniques for identifying both networks: DP/MAS gives the chemical composition of the lightly cross-linked network under conditions where the more heavily

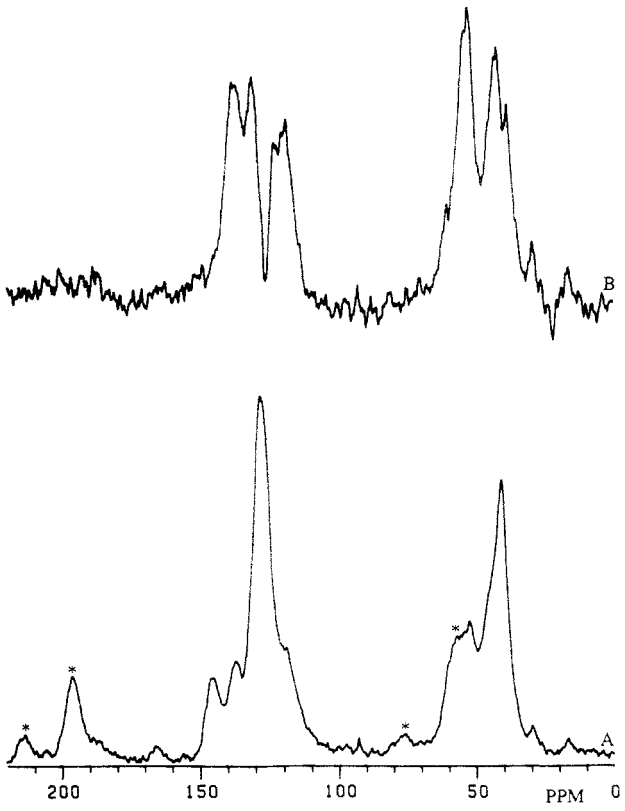

Figure 5. CP/MAS spectra of (A) PS/VI IPN and (B) the subtraction of the spectrum of polystyrene from that of PS/VI IPN.

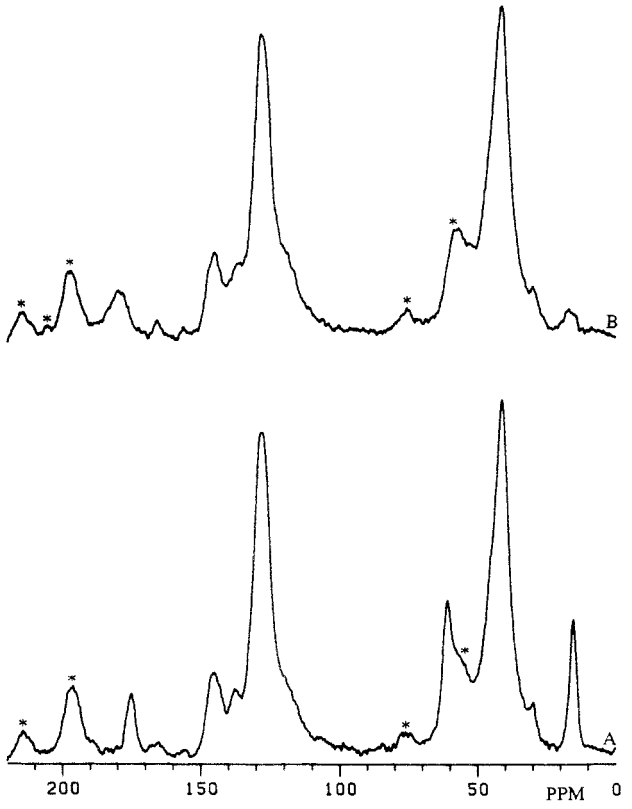

Figure 6. CP/MAS spectra of (A) PS/VI–EA and (B) PS/VI–acid IPNs.

cross-linked network is transparent; the latter is then identified by CP/MAS. Combining the spectra with elemental analyses allows for an unambiguous determination of the ligands present.

DP/MAS spectra of network I swollen in the monomers of network II show that both monomers of the second network are sorbed from solution into the polystyrene beads. CP/MAS spectra show that the desired networks have been formed.

Ligand accessibility and completeness of reaction are also defined by the NMR: spectra of acrylate-containing IPNs which have been hydrolyzed with KOH indicate that cleavage of all ester sites occurs with no apparent degradation of the network. Solid-state ^{13}C NMR spectroscopy is thus found to be a very useful and readily applied technique for the characterization of IPNs.

Acknowledgment. We gratefully acknowledge support from the Department of Energy, Office of Basic Energy Sciences, through Grant DE-FG05-86ER13591. Contributions to the synthesis by Dr. A. Trochimczuk and Ms. C. G. Ciaccio are also acknowledged.

References and Notes

(1) Sperling, L. H. *J. Polym. Sci. Macromol. Rev.* **1977**, *12*, 141.
(2) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.
(3) Sperling, L. H. *Polym. Eng. Sci.* **1985**, *25*, 517.
(4) Frisch, K. C.; Klempner, D.; Xiao, H. X.; Cassidy, E.; Frisch, H. L. *Polym. Eng. Sci.* **1985**, *25*, 758.
(5) Sperling, L. H. *CHEMTECH* **1988**, *18*, 104.
(6) Alexandratos, S. D. *Sep. Purif. Methods* **1992**, *21*, 1.
(7) Axelson, D. E.; Russell, K. E. *Prog. Polym. Sci.* **1985**, *11*, 221.
(8) Andreis, M.; Koenig, J. L. *Adv. Polym. Sci.* **1989**, *89*, 69.
(9) Stover, H. D. H.; Frechet, J. M. J. *Macromolecules* **1991**, *24*, 883.
(10) Mohanraj, S.; Ford, W. T. *Macromolecules* **1985**, *18*, 351.
(11) Ford, W. T.; Mohanraj, S.; Blossey, E. C. *Macromol. Synth.* **1990**, *10*, 91.
(12) Doskocilova, D.; Schneider, B. *Chem. Phys. Lett.* **1970**, *6*, 381.
(13) Doskocilova, D.; Schneider, B.; Jakes, J. *J. Magn. Reson.* **1978**, *29*, 79.
(14) Stover, H. D. H.; Frechet, J. M. J. *Macromolecules* **1989**, *22*, 1574.
(15) McDonald, C. J.; Smith, P. B.; Roper, J. A.; Lee, D. I.; Galloway, J. G. *Colloid Polym. Sci.* **1991**, *269*, 227.
(16) Ku, W. H.; Liang, J. L.; Wei, K. T.; Liu, H. T.; Huang, C. S.; Fang, S. Y.; Wu, W. G. *Macromolecules* **1991**, *24*, 4605.
(17) Huelck, V.; Thomas, D. A.; Sperling, L. H. *Macromolecules* **1972**, *5*, 340. Donatelli, A. A.; Sperling, L. H.; Thomas, D. A. In *Recent Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum: New York, 1974.
(18) Alexandratos, S. D.; Grady, C. E.; Crick, D. W. *Macromolecules* **1991**, *24*, 6365.
(19) Earl, W. L.; VanderHart, D. L. *J. Magn. Reson.* **1982**, *48*, 35.
(20) Ivin, K. J.; Pitchumani, S.; Reddy, C. R.; Rajadurai, S. *Eur. Polym. J.* **1981**, *17*, 341.
(21) Watts, D. C. *J. Biomed. Mater. Res.* **1979**, *13*, 423.
(22) Prosser, H. J.; Richards, C. P.; Wilson, A. D. *J. Biomed. Mater. Res.* **1982**, *16*, 431.
(23) Boulton, A. J.; McKillop, A. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Ed.; Pergamon: New York, 1984; Vol. 2, pp 29–65.
(24) Grimmett, M. R. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1980; Vol. 27, pp 241–326.
(25) Treibs, A. *Liebigs Ann. Chem.* **1932**, *497*, 297.
(26) Kost, A. N.; Gromov, S. P.; Sagitullin, R. S. *Tetrahedron* **1981**, *37*, 3423.
(27) Begtrup, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 521.
(28) Ghesquiere, D.; Chachaty, C.; Tsutsumi, A. *Macromolecules* **1979**, *12*, 775.
(29) Dambatta, B. B.; Ebdon, J. R.; Huckerby, T. N. *Eur. Polym. J.* **1984**, *20*, 645.
(30) Konishi, K.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2512.
(31) Begtrup, M. *Acta Chem. Scand., Ser. B* **1974**, *28*, 61.