Macromolecules **2008,** *41,* 387−389

Chain Structure of Substituted Stilbene−Maleic Anhydride Alternating Copolymer Probed by Solid-State NMR

Min Mao, Chul Kim, Sungsool Wi,* and S. Richard Turner*

Department of Chemistry, Macromolecules and Interfaces Institute (MII), Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0344

Received September 17, 2007; Revised Manuscript Received November 2, 2007

ABSTRACT: Double-quantum heteronuclear local field solid-state NMR spectroscopy (2Q-HLF solid-state NMR) has been employed to investigate the chain structure of *N*,*N*,*N*′,*N*′-tetraethyl-4, 4′-diaminostilbene (TDAS) and ^{13}C labeled maleic anhydride (MA) alternating copolymer. The torsional angle of the H−^{13}C−^{13}C−H part of the anhydride ring was found to be 0°, indicating an all cis configuration of the H−^{13}C−^{13}C−H moiety of the anhydride ring. After hydrolysis of the anhydride groups and protonation of the amino groups, the torsional angle of the H−^{13}C−^{13}C−H moiety of the hydrolyzed anhydride groups appears to be 60°, indicating significant rotation of the polymer backbone. Because of the predominately cis configuration of the H−^{13}C−^{13}C−H part of the anhydride ring, the diethylamino phenyl groups are concentrated on the two sides of the backbone plane and the anhydride groups are in the backbone plane.

Functional polymers[1] carrying reactive functional groups that can participate in chemical processes have tremendous applications in a great variety of areas such as organic electronics,[2] polymer−drug conjugates,[3,4] and biomaterials.[5] The reactive groups can be incorporated along the main chain as pendant groups or as multiple chain ends in star or dendritic molecules. Because of the tolerance of the free radical polymerization process to functional groups, free radical polymerization is one of the most widely used methods for preparing functional polymers.

Alternating free radical polymerization with multisubstituted monomers is a convenient and powerful tool to construct highly functional polymeric materials.[6] Multisubstituted monomers have the potential to raise the functionality density along the backbone and thus to increase the functional group concentration. Although multisubstituted monomers usually cannot form homopolymers, many of them can be polymerized via so-called "alternating free radical polymerization".[6−10] Highly functional alternating copolymers can be produced by using functional electron-rich (donor) and electron-poor (acceptor) monomer pairs.[11,12] The type of functional group, molecular weight, polymer architecture, the density of functional groups, and stiffness of the polymer chain can be controlled using this strategy. Because of the alternating nature of the alternating free radical polymerization, regular placement of functional groups along the backbone, important for certain applications,[13] is possible.

Solution NMR has been employed to investigate the chain configuration of many alternating copolymers since cis and trans configurations should have different ^{1}H and ^{13}C NMR signals. Olson and Butler used ^{13}C NMR spectroscopy to investigate the stereochemistry of the *N*-phenyl maleimide−2-chloroethyl vinyl ether alternating copolymers to elucidate the mechanism of the alternating free radical polymerization.[14−17] After comparing the ^{13}C NMR spectra of the polymers with the corresponding model compounds, they concluded that the succinimide units mainly adopt the cis configuration indicating the significant participation of a donor−acceptor complex or "charge-transfer complex" in the alternating copolymerization. However ^{15}N NMR spectroscopy of alkene−*N*-methyl maleimide copolymers and ^{13}C NMR spectroscopy of alkene−maleic anhydride copolymers showed mostly trans enchainment of the maleimide units.[18−20] All of the above studies relied on the comparison between the NMR spectra of model compounds and the polymers, where it is inherently difficult to assign the NMR signals correctly due to the broad signal, signal overlap, and small chemical shift differences.

During the past decade, tremendous progress in solid-state NMR technique has made this technique valuable for the study of polymer structure.[21−23] Double-quantum solid-state NMR has been successfully used to determine the gauche/trans chain configurations of various polymers.[24,25] The torsional angle of isotopically labeled peptide segments also can be measured by solid-state NMR.[26,27] Among numerous solid-state NMR methods, double-quantum heteronuclear local field solid-state NMR spectroscopy (2Q-HLF solid-state NMR), developed by Levitt 10 years ago, is able to measure the torsional angle of a $^{13}C_2$-labeled H−C−C−H moiety with a resolution of ≈±20° in the neighborhood of the cis configuration and ≈±10° in the neighborhood of the trans configuration.[27,28] This technique is well suited for the study of the chain configuration in alternating copolymers avoiding the difficulties of solution NMR studies to determine the backbone stereochemistry. For this study, the *N*,*N*,*N*′,*N*′-tetraethyl-4, 4′-diaminostilbene (TDAS) and maleic anhydride (MA) alternating copolymer was synthesized using ^{13}C-labeled maleic anhydride and characterized following the procedure described elsewhere (Scheme 1).[11]

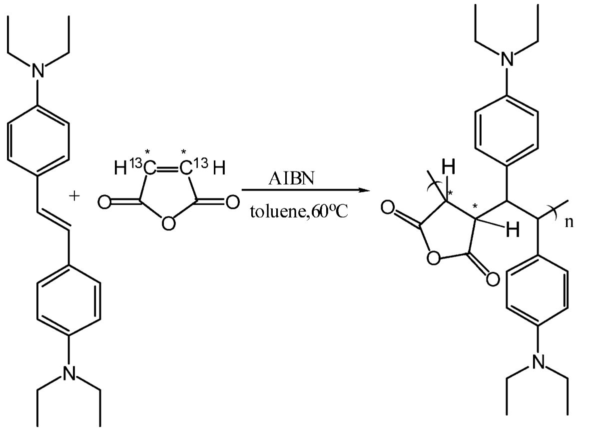
HCCH-2Q-HLF solid-state NMR exploits the evolution of the excited double-quantum coherence between the neighboring ^{13}C spins in the presence of local heteronuclear ^{1}H−^{13}C dipolar fields from the directly bonded ^{1}H spins.[27] The pulse sequence for the HCCH-2Q-HLF experiment is shown in Figure 1A. After the cross-polarization pulse and a 90° pulse, the homonuclear recoupling sequence $R26_4^{11}$ creates double-quantum coherences which evolve under ^{1}H−^{13}C dipolar couplings while suppressing ^{1}H−^{1}H dipolar couplings for a fraction of a rotation period (t_1). Then double-quantum coherences are reconverted to observable ^{13}C magnetization by a second $R26_4^{11}$ block,

---

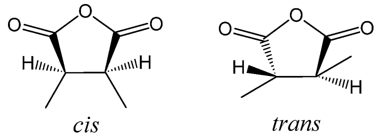
* To whom correspondence should be addressed.

10.1021/ma702089e CCC: $40.75

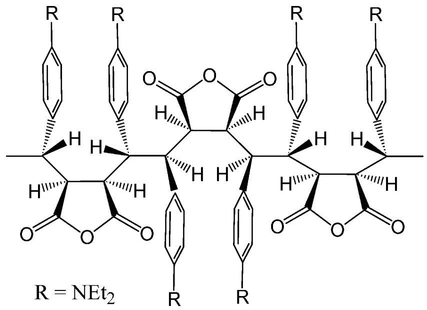
Scheme 1. The Synthesis of ^{13}C-labeled TDAS−MA Alternating Copolymer



Scheme 2. Two Possible Enchainment Modes (cis and trans) of the Anhydride Units



Scheme 3. Possible Chain Configuration and Spatial Arrangement of the Functional Groups of the TDAS−MA Alternating Copolymer



with a standard double-quantum filtering phase cycle, followed by a 90° pulse. The experiments were performed at a magnetic field of 7.1 T and under magic-angle-spinning with spinning frequency $\nu_r = 3673$ Hz. The amplitude and duration of the double-quantum excitation block $R26_4^{11}$ is 23.87 kHz ($= 6.5\ \nu_r$) and 1.09 ms ($= 4\ \tau_r$, where τ_r is the spinning rotor period). The maximum frequency-switched Lee−Goldburg (FSLG) off-resonance (^{1}H offset frequency $= \pm 63.64$ kHz; rf-pulse power $\nu_{rf} = 90$ kHz) spin-locking period to suppress ^{1}H−^{1}H homonuclear dipolar interaction during the double-quantum evolution period is 1 τ_r, which is 15 times a t_1 increment that corresponds to a basic FSLG unit, $(9.07\ \mu s)_0(9.07\ \mu s)_{180}$, where 0 and 180 designate the rf-pulse phase (in degrees) of FSLG spin-locking pulse irradiation. The proton decoupling powers during the $R2\,6_4^{11}$ block and two-pulse phase modulated (TPPM) decoupling scheme[29] for signal acquisition are 80 kHz and 66 kHz, respectively. A total of 2048 transient signals were accumulated for each t_1 slice with acquisition delay for 2s on 30 mg of ^{13}C-labeled samples.

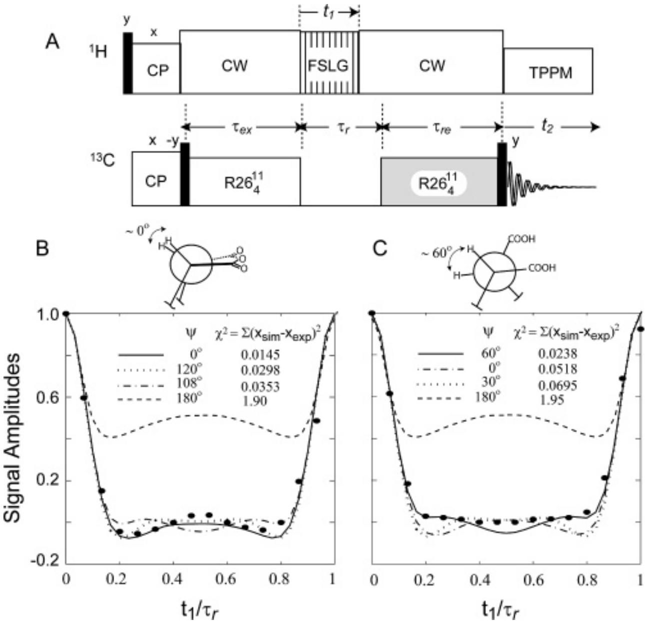
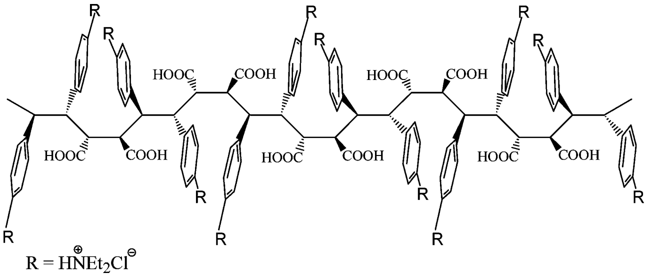


Figure 1. Pulse sequence for HCCH-2Q-HLF experiment (A), and experimental data and simulations for the $^{13}C_2$-labeled TDAS−MA alternating copolymer (B) and the hydrolyzed $^{13}C_2$-labeled TDAS−MA alternating copolymer (C) samples. A standard FSLG scaling factor, $k = 0.57$, has been used for our simulations. Simulation results with torsion angles of 0° and 60° provide the best fit to the experimental data of the $^{13}C_2$-labeled TDAS−MA alternating copolymer (B) and the hydrolyzed $^{13}C_2$-labeled TDAS−MA alternating copolymer (C), respectively, as expected.

Two possible enchainment modes (cis and trans) of the anhydride units are shown in Scheme 2. The torsional angle of the H−^{13}C−^{13}C−H part of the anhydride ring is 0° (Figure 1B), indicating the predominately cis configuration of the H−^{13}C−^{13}C−H linkage of the anhydride ring. Considering the ±20° resolution of the torsional angle measurement of the 2Q-HLF solid-state NMR method, at least 80% of the H−^{13}C−^{13}C−H part of the anhydride ring adopts the cis configuration. Olson and Butler have claimed that the cis configuration results from the direct copolymerization of a charge-transfer complex of the donor and acceptor comonomers.[14−17,30] Because of strong steric hindrance, the two bulky substituted phenyl groups of the stilbene should mainly adopt the trans configuration. On the basis of this assumption, a possible picture of the chain configuration of the TDAS−MA alternating copolymer is shown in Scheme 3: the polymer backbone is highly kinked due to the predominately cis configuration of the H−^{13}C−^{13}C−H part of the anhydride ring. With such a structure, the functional groups are arranged in a regular way, i.e., the diethylamino phenyl groups are on the two sides of the backbone plane and the anhydride groups are within the backbone plane. This spatial arrangement of functional groups along the backbone may open up opportunities for modification reactions that can lead to unique polymers with potentially useful properties. Currently we are actively pursuing targets derived from these structures.

When the amino groups are protonated and charged, they will experience strong electrostatic repulsion. If the above picture of the chain configuration of the TDAS−MA copolymer is correct, the electrostatic repulsion between the charged amino groups will rotate the polymer backbone to minimize the unfavorable repulsion, since they are concentrated on both sides on the polymer backbone plane (Scheme 4). When the anhydride ring is opened, such rotation of the polymer backbone will be possible and the torsional angle of the H−^{13}C−^{13}C−H moiety of the hydrolyzed anhydride will be changed. Dihedral angle measurement of the hydrolyzed TDAS−MA copolymer is consistent with this hypothesis. The ^{13}C-labeled TDAS−MA copolymer was hydrolyzed in dilute HCl solution. The hydrolysis of the anhydride ring was confirmed by the disappearance of the peaks from the anhydride groups (1841 and 1772 cm^{-1}) and appearance of a strong absorption peak associated with the

Scheme 4. Possible Chain Configuration and Spatial Arrangement of the Functional Groups of the Hydrolyzed TDAS−MA Alternating Copolymer



free carboxylic acid (1721 cm^{-1}) in the IR spectrum. The HCCH-2Q-HLF solid-state NMR spectrum of the dried hydrolyzed ^{13}C-labeled TDAS−MA copolymer is shown in Figure 1C. The torsional angle of the H−^{13}C−^{13}C−H moiety of the hydrolyzed anhydride groups appears to be 60°, indicating the significant rotation of the polymer backbone and gauche configuration for the H−^{13}C−^{13}C−H moiety of the hydrolyzed anhydride.

In conclusion, the result of the solid-state NMR torsional angle measurement of the TDAS−MA copolymer has shown that the H−^{13}C−^{13}C−H linkages in the maleic anhydride units are enchained in a predominately cis configuration. This results in a chain structure that positions the diethylamino phenyl groups in an alternating arrangement on both sides of the plane of the backbone with the anhydride groups within the backbone plane. When the anhydride groups are hydrolyzed, there is a 60° rotation of the H−^{13}C−^{13}C−H linkage in the maleic anhydride units. Our continuing studies include reacting the anhydride groups to precisely place various functional groups along the backbone and structure analysis of other examples of these stilbene copolymers.

Acknowledgment. Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

References and Notes

(1) Fréchet, J. M. J. *Science* **1994**, *263*, 1710−1715.
(2) Fréchet, J. M. J. *Prog. Polym. Sci.* **2005**, *30*, 844−857.
(3) Khandare, J.; Minko, T. *Prog. Polym. Sci.* **2006**, *31*, 359−397.
(4) Duncan, R. *Nature Rev.* **2003**, *2*, 347−360.
(5) Mammen, M.; Choi, S. K.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2754−2794.
(6) Turner, S. R.; Anderson, C. C.; Kolterman, K. M. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 253−258.
(7) Zhang, X.; Li, Z. C.; Li, K. B.; Lin, S.; Du, F. S.; Li, F. M. *Prog. Polym. Sci.* **2006**, *31*, 893−948.
(8) Hall, H. K.; Padias, A. B. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2845−2858.
(9) Hall, H. K.; Padias, A. B. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2069−2077.
(10) Rzaev, Z. M. O. *Prog. Polym. Sci.* **2000**, *25*, 163−217.
(11) Mao, M.; Turner, S. R. *Polymer* **2006**, *47*, 8101−8105.
(12) Mao, M.; Turner, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 3832−3833.
(13) Wulff, G.; Schauhoff, S. *J. Org. Chem.* **1991**, *56*, 395−400.
(14) Olson, K. G.; Butler, G. B. *Macromolecules* **1983**, *16*, 707−710.
(15) Butler, G. B.; Olson, K. G.; Tu, C. L. *Macromolecules* **1984**, *17*, 1884−1887.
(16) Olson, K. G.; Butler, G. B. *Macromolecules* **1984**, *17*, 2480−2486.
(17) Olson, K. G.; Butler, G. B. *Macromolecules* **1984**, *17*, 2487−2501.
(18) Komber, H.; Jakisch, L.; Zschoche, S.; Mobus, H.; Ratzsch, M.; Scheller, D. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 547−552.
(19) Ratzsch, M.; Zschoche, S.; Steinert, V.; Schlothauer, K. *Makromol. Chem.* **1986**, *187*, 1669−1679.
(20) Komber, H. *Makromol. Chem. Phys.* **1995**, *196*, 669−678.
(21) Duer, M. J., Ed. *Solid-State NMR Spectroscopy Principles and Applications*; Blackwell Science Ltd: Oxford, U.K., 2002.
(22) Schmidt-Rohr, K., Spiess, H. W., Eds. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, U.K., 1994.
(23) Spiess, H. W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5031−5044.
(24) Harris, D. J.; Bonagamba, T. J.; Hong, M.; Schmidt-Rohr, K. *Polymer* **2005**, *46*, 11737−11743.
(25) Schmidt-Rohr, K.; Hu, W.; Zumbulyadis, N. *Science* **1998**, *280*, 714−717.
(26) Wi, S.; Sun, H.; Oldfield, E.; Hong, M. *J. Am. Chem. Soc.* **2005**, *127*, 6451−6458.
(27) Feng, X.; Eden, M.; Brinkmann, A.; Luthman, H.; Eriksson, L.; Graslund, A.; Antzutkin, O. N.; Levitt, M. H. *J. Am. Chem. Soc.* **1997**, *119*, 12006−12007.
(28) Feng, X.; Lee, Y. K.; Sandstrom, D.; Eden, M.; Maisel, H.; Sebald, A.; Levitt, M. H. *Chem. Phys. Lett.* **1996**, *257*, 314−320.
(29) Benett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *J. Chem. Phys.* **1995**, *103*, 6951−6958.
(30) Mulliken, R. S.; Person, W. B. *Molecular Complex: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.

MA702089E