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THE TRIAD DISTRIBUTION AND THE *cis/trans* CONFIGURATIONS AT THE CYCLIC MALEIC ANHYDRIDE UNITS IN MALEIC ANHYDRIDE-STYRENE COPOLYMERS PREPARED IN *N,N*-DIMETHYLFORMAMIDE

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ABSTRACT

The monomer unit sequence distribution and the *cis/trans* linkage configurations of maleic anhydride units in maleic anhydride (Ma)-styrene (St) copolymers prepared in *N,N*-dimethylformamide with *N,N'*-azobisisobutyronitrile at 50°C over a wide range of Ma monomer feed mole fractions were determined using DEPT ^{13}C-NMR spectroscopy. It was found that when the Ma feed mole fraction is more than 0.4, the monomer unit sequence becomes almost alternating and the mole fraction of the *cis* linkages at the Ma units in the copolymer attain a nearly defined maximum value of 0.54 ± 0.06.

INTRODUCTION

Maleic anhydride (Ma) and styrene (St) are well known to form strongly alternating copolymers. Many studies have shown the participation of both free monomers and the comonomer donor–acceptor (DA) complex in the propagation step [1, 2].

O'Donnel, Hill, et al. [3, 4] reported the sequence distribution of Ma–St copolymers using DEPT ^{13}C-NMR spectroscopy. Butler et al. [5–8] examined the linkage configurations of Ma–St copolymers as well as copolymers of *N*-substituted maleimides and vinyl ethers and proposed that the correlation between the alternation and the stereo-regularity in copolymers would imply an important aspect for the propagating mechanism [8–10].

In the copolymerizations of Ma with St and with *p*-methoxy styrene, Brown et al. [11, 12] confirmed the strong relationship between the alternation of comonomer units and the linkage configurations at the cyclic Ma monomer units even in such a polar solvent as methyl ethyl ketone (MEK). A participation of the electron donor-acceptor (DA) complexes was suggested as the most likely mechanism. Since polarity of the solvent would play an important role in the copolymerizations that involve DA complexes, this study focuses on the determination of the sequence distribution and the content of the *cis/trans* configurations at the cyclic Ma units in Ma–St copolymers prepared in an extremely polar solvent, *N,N*-dimethylformamide (DMF).

EXPERIMENTAL

St (Ajax) proved its purity of ≥99.5% by ^{1}H-NMR spectroscopy and was used as supplied. Ma (Ajax) was recrystallized from dried benzene (by sodium wires). *N,N'*-azobisisobutyronitrile (AIBN) (Riedel-de-Haen) was recrystallized from methanol. DMF (Fluka), assay ~99% (GC), was dried over molecular sieves type A4 (Ajax) [13]. Acetone was distilled and kept over molecular sieves. Diethyl ether (DEE) (BDH) was dried over Na wires.

All polymerization were carried out in DMF with a total monomer concentration of 4.000 ± 0.001 mol/L, an initiator (AIBN) concentration of 0.0305 ± 0.0001 mol/L at a temperature of 50.0 ± 0.1°C. Ma, AIBN, a small amount of hydroquinone ($< 3 \times 10^{-3}$ mol/L) to inhibit the polymerization before the reaction mixture is ready for polymerization [4], and St were weighed and placed in a glass ampule. DMF was then added to make up a total volume of 10.00 ±0.02 mL. The ampule was sealed under vacuum after repeated freeze-degas-thaw procedures. The polymerization was carried out in an oil thermostat. The ampule was shaken well throughout the reaction. The conversion was less than 10% in general and less than 5% when the monomer composition in the feed was $f_{Ma} \leq 0.2$ or was $f_{Ma} \geq 0.8$. The polymerization proceeded in homogeneous DMF solutions. The polymerization was stopped by precipitating the copolymer into a large amount of DEE. The copolymer was collected on a No. 4 sintered glass filter,dissolved in a small amount of acetone, and reprecipitated in DEE. The copolymer was then dried in a desiccator under vacuum at room temperature for about 20 hours.

Solutions of copolymers in acetone-d_6 was prepared to the concentration of 0.08–0.19 w/w (g copolymer/g acetone) in precision NMR tubes. A Bruker AC-300 NMR spectrometer was used for running the ^{13}C-NMR and DEPT ^{13}C-NMR experiments [14] at 75.46 MHz with a broad band ^{1}H dual 5 mm probe over 15 to 20 hour periods at 308 K (35°C). The ^{1}H decoupler- and the ^{13}C-$\pi/2$ pulse times were set at 9.9 and 4.2 μs respectively with a 2-second recycle delay. The J modulation time was set to 3.5 ms, equivalent to $J = 142.86$ Hz ($\Delta = 0.5/J$ for optimum polarization /

sensitivity). DEPT FID-acquired spectra were transformed and generated by linear combination for DEPT subspectra. The *linesim* [15] simulation program was then run for DEPT subspectra of methylene C1 and methine C3 for obtaining the triad fraction data (F_{010}, $F_{(011+110)}$, F_{111}) and the amounts of the *cis* and *trans* linkage configurations, respectively.

RESULTS AND DISCUSSION

The copolymer samples were prepared for a wide range of Ma feed monomer compositions of $f_0 = 0.05$–0.9. Because Ma(0) does not homopropagate [16], the St(1) centered triads are used for determining the triad sequence distribution. The peak assignment in Fig. 1 was taken according to Butler et al. [8], and that for DEPT ^{13}C-NMR subspectra of methylene C1 was by Baron et al. [3] and by Brown et al. [11, 17–19]. The chemical shifts of St(1) centered triads were taken from methylene DEPT subspectra of C1 (Fig. 2) as follows:

Triad	Sequence	Chemical shift
010	Alternating	33–37 ppm
011 + 110	Semialternating	37–42
111	Nonalternating	42–47

Triad mole fractions (F_{010}, $F_{(011+110)}$, F_{111}) of the copolymers were determined from the peak areas and are shown in Fig. 3. In Fig. 3 and in subsequent figures, interpreted best fit lines are drawn in order to indicate the trends of the data. The DEPT methylene C1 subspectra (Fig. 2) clearly shows increasing alternation in copolymers when the copolymers were prepared with the Ma feed monomer composition of $f_0 = 0.05$–0.35. Even in very polar DMF solution, the resulting copolymers were found to have almost alternating sequences ($F_{010} = 1$) when the feed Ma fraction (f_0) was greater than 0.4 with $F_{(011+110)}$ and F_{111} decreasing to be very close to zero.

The mole fractions of St(1) and Ma(0) units, F_1 and F_0, respectively, in the copolymers are calculated from the triad fractions according to the equation [3]

$$\frac{F_1}{F_0} = 1 + \frac{2F_{111} + \mathrm{F}_{(011+110)}}{2F_{010} + F_{(011+110)}}, \qquad \text{where } F_0 + F_1 = 1$$

Figure 4 presents the variation of the Ma mole fraction of Ma–St copolymers with respect to the feed composition. It shows clearly that the alternating trend of the composition curve (F_0 vs f_0) is very similar to that of the alternating triad fraction curve (F_{010} vs f_0) in Fig. 3. The Ma composition in copolymers (F_0) increases with increasing Ma composition in the feed (f_0) when $f_0 = 0.05$–0.35 and reaches a constant value of $F_0 \simeq 0.5$ when the feed Ma fraction is around 0.4.

The amount of *cis/trans* linkage configurations at the cyclic Ma units in the copolymers was determined from the methine (CH) subspectra for C3 (51–54 ppm) [8], where the *cis* C3 peaks appeared at 51.5 ± 0.1 ppm while the *trans* C3 peaks appeared at 52.5 ± 0.1 ppm. The peak areas were determined by the *linesim* peak simulation method and the results were further confirmed by the paper-cutting method. Figure 5 shows the relationship between the amount of the *cis* linkage configuration at the Ma units and the feed composition from which the copolymers were formed. The amount of the *cis* configurations (F_{cis}) increases along with the

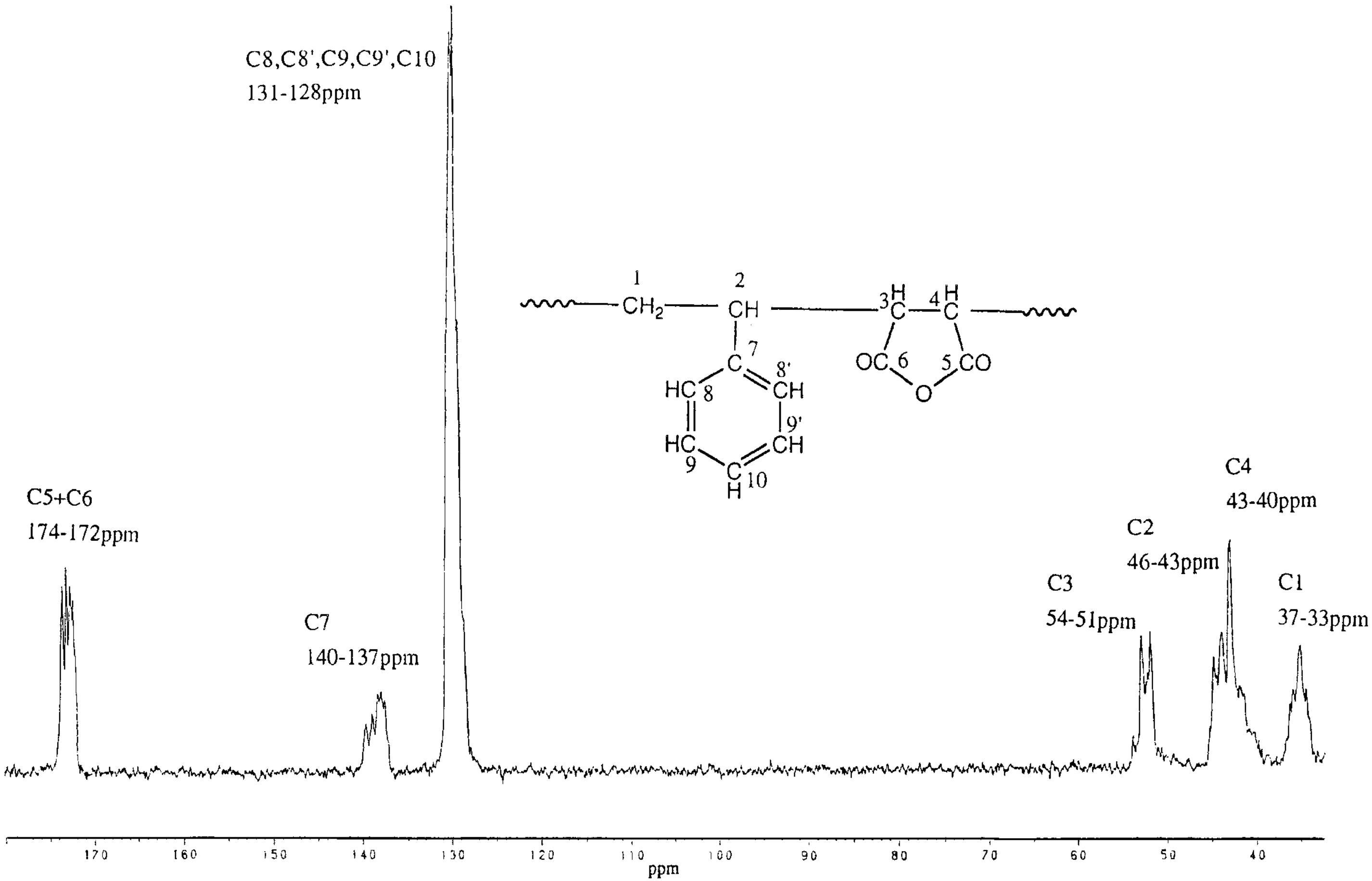

FIG. 1. Typical ^{13}C-NMR spectrum of Ma–St copolymer prepared in DMF at 50°C. Ma monomer feed composition $f_0 = 0.5$.

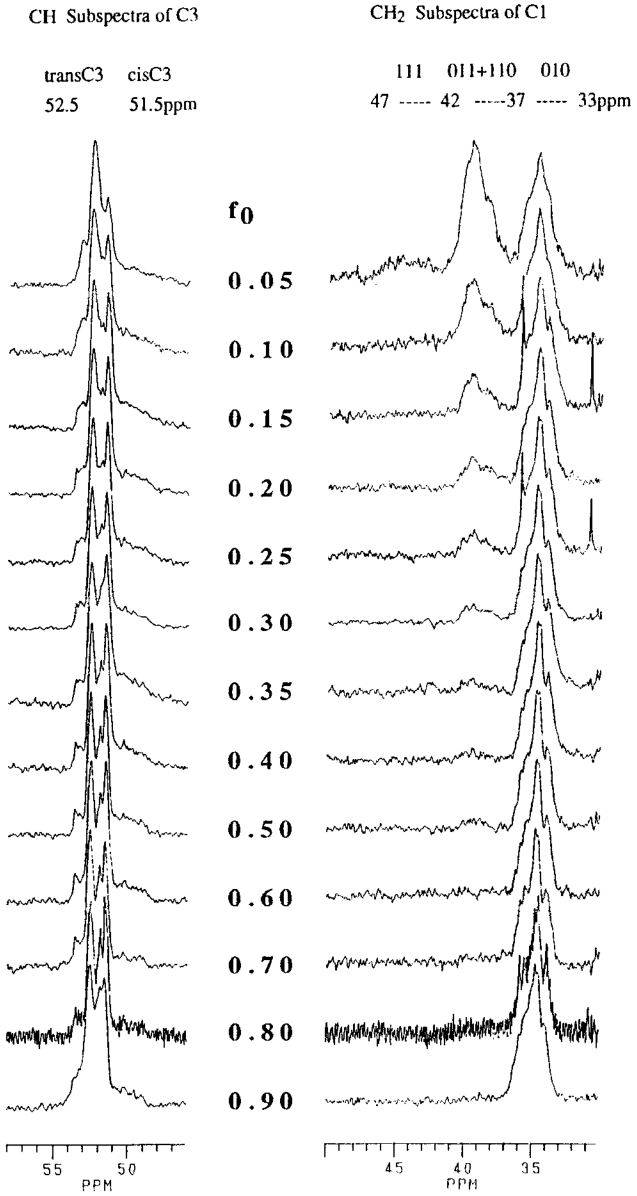

FIG. 2. DEPT ^{13}C-NMR subspectra of methine CH (C3) and methylene CH_2 (C1) of Ma(0)-St(1) copolymers prepared in DMF at 50°C. Ma mole fraction in monomer feed ranges from f_0 = 0.05 to 0.9.

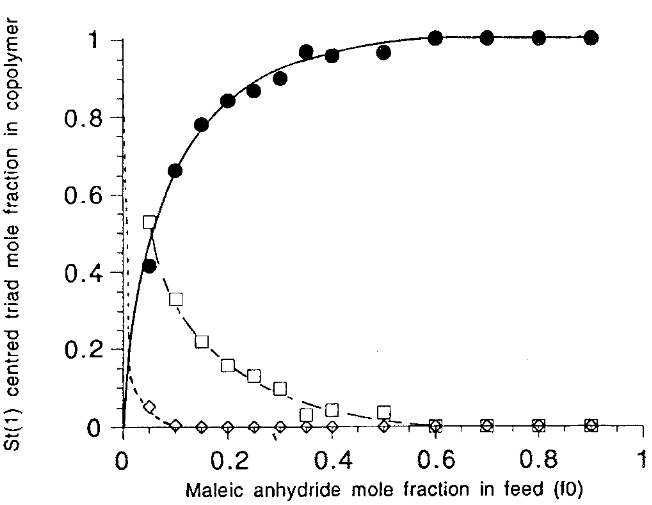

FIG. 3. St(1) centered triad mole fraction of Ma(0)-St(1) copolymer prepared in DMF at 50°C. [Ma + St] = 4.000 ± 0.001 mol/L. [AIBN] = 0.0305 ± 0.0001 mol/L. (●) $F(010)$, (□) $F(011 + 110)$, (◇) $F(111)$.

Ma composition in the feed (f_0) and reaches a nearly defined value of 0.54 ± 0.06 when f_0 is around 0.4 in a closely correlated manner as the alternating sequences increase as shown in Fig. 3.

There is a remarkable coincidence between the extent of the alternation in Fig. 3 and the amount of the *cis* linkage configurations in Fig. 5. When the copolymer is almost alternating, the amount of *cis* configurations also reaches a nearly constant

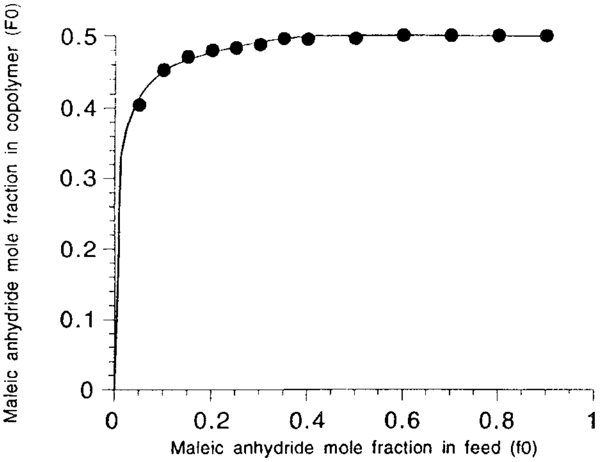

FIG. 4. The copolymer composition diagram of Ma(0)-St(1) copolymers prepared in DMF at 50°C. [Ma + St] = 4.000 ± 0.001 mol/L. [AIBN] = 0.0305 ± 0.0001 mol/L.

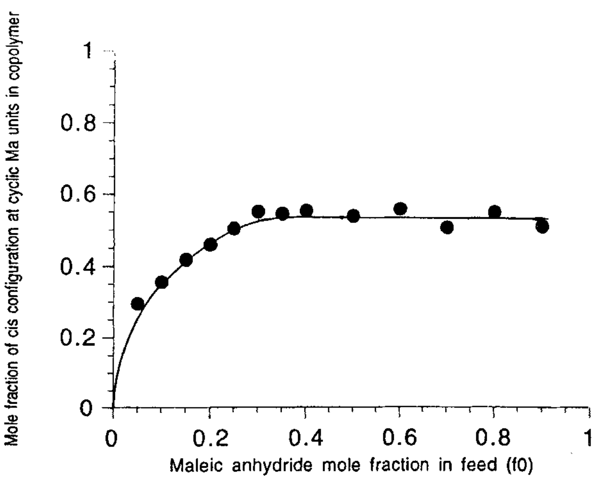

FIG. 5. Mole fraction of the *cis* linkage configurations at the cyclic Ma units in Ma-St copolymers prepared in DMF at 50°C. [Ma + St] = 4.000 ± 0.001 mol/L. [AIBN] = 0.0305 ± 0.0001 mol/L.

maximum value with more than half the linkages at the Ma units being *cis* configurations. This indicates a link between the alternating tendency and the resulting stereoregularity of monomer units. A mechanism in which a propagating St radical attacks the Ma side of a 1:1 Ma-St donor-acceptor complex at either an edge on position or at an orthogonal position of the complex [12], followed by a concerted addition of the St monomer in the complex, may provide an explanation for the remarkably large proportion of the *cis* linkage configuration.

While the bootstrap model [20, 21] and the penultimate model [22] are useful in recognizing the effect of local monomer concentrations around a growing polymer radical and the effect of the second last unit of a growing radical, respectively, both mechanisms are essentially based on additions of free monomers. Since radical reactions are susceptible to steric hindrance, addition of free monomers to the growing Ma radicals would overwhelmingly create *trans* linkage configurations at the Ma units.

CONCLUSION

There appears to be a close correlation between the formation of an alternating monomer unit sequence and the formation of a *cis* linkage configuration at Ma units in the copolymers of Ma and St prepared in even such a very polar solvent as DMF. Almost alternating copolymers are obtained when the feed Ma fraction is around 0.4 or higher, with the amount of the *cis* linkage configuration reaching a maximum of 54 ± 6%. Such a large proportion of the *cis* linkage configuration may be conveniently explained by a participation of the 1:1 donor-acceptor complex of Ma and St.

REFERENCES

[1] J. M. G. Cowie, *Alternating Copolymers*, Plenum Press, New York, 1985.

[2] D. J. T. Hill, J. H. O'Donnel, and P. W. O'Sullivan, *Prog. Polym. Sci., 8*, 215 (1982).

[3] P. F. Baron, D. J. T. Hill, J. H. O'Donnel and P. W. O'Sullivan, *Macromolecules, 17*, 1967 (1984).

[4] D. J. T. Hill, J. H. O'Donnel, and P. W. O'Sullivan, *Ibid., 18*, 9 (1985).

[5] K. G. Olson and G. B. Butler, *Ibid., 16*, 707 (1983).

[6] K. G. Olson and G. B. Butler, *Ibid., 17*, 2480 (1984).

[7] K. G. Olson and G. B. Butler, *Ibid., 17*, 2486 (1984).

[8] G. B. Butler, C. H. Do, and M. C. Zerner, *J. Macromol. Sci.—Chem., A26*(8), 1115 (1989).

[9] G. B. Butler, K. G. Olson, and C. L. Tu, *Macromolecules 17*, 1884 (1984).

[10] G. B. Butler and C. H. Do, *Makromol. Chem., Suppl. 15*, 93 (1989).

[11] P. G. Brown and K. Fujimori, *Makromol. Chem., Rapid Commun., 15*, 61 (1994).

[12] P. G. Brown and K. Fujimori, *Polymer, 36*, 1053 (1995).

[13] D. R. Burfield and R. H. Smithers, *J. Org. Chem., 43*, 3966 (1978).

[14] D. T. Pegg, D. M. Doddrell, and M. R. Bendall, *J. Chem. Phys., 77*, 2745 (1982).

[15] P. F. Baron, *linesim*, version 880 601, Bruker (Australia) Pty. Ltd., Sydney, 1988.

[16] B. C. Trivedi and B. M. Culberton, *Maleic Anhydride*, Plenum Press, New York, 1982, p. 239.

[17] P. G. Brown, K. Fujimori, and D. J. Tucker, *Polym. Bull. (Berlin), 27*, 543 (1992).

[18] P. G. Brown and K. Fujimori, *Ibid., 29*, 85 (1992).

[19] P. G. Brown, K. Fujimori, A. S. Brown, and D. J. Tucker, *Makromol. Chem., 194*, 1357 (1993).

[20] B. Klumperman and P. G. Brown, *Macromolecules, 27*, 6100 (1994).

[21] B. Klumperman and I. R. Kraeger, *Ibid., 27*, 1529 (1994).

[22] E. Merz, T. Alfred Jr., and G. Goldfinger, *J. Polym. Sci., 1*, 75 (1946).

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