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Copolymerization of Maleic Anhydride and Thiophene

A. CARDON and E. J. GOETHALS

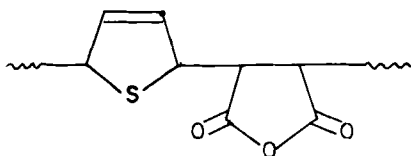
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SUMMARY

Mixtures of maleic anhydride and thiophene were polymerized to alternating copolymers under the influence of azobisisobutyronitrile. The yield and molecular weight were highest when equimolar amounts of both monomers were used. Through comparison of the NMR spectrum of the copolymer with the NMR spectra of 2,3-dihydrothiophene and 2,5-dihydrothiophene, the copolymer proposed consists mainly of the following structure:



It is believed that polymerization occurs via a charge-transfer complex.

INTRODUCTION

It has been shown by several authors that copolymerization of two monomers which form a charge-transfer complex with each other proceeds

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smoothly, leading to alternating copolymers in high yields [1, 2]. Recently Otsu and Inoue [3] studied the copolymerization of several alkyl vinyl sulfides with maleic anhydride (MAN) and also detected the existence of charge-transfer complexes between the two comonomers. The same phenomena were observed by us in the case of cyclic unsaturated sulfides [4]. Thiophene also forms a charge-transfer complex with maleic anhydride [5]. Although thiophene is normally not capable of undergoing vinyl polymerization, the present work involves an investigation to determine whether the existence of such a complex would lead to the formation of alternating copolymers.

RESULTS AND DISCUSSION

Polymerization

When a solution of thiophene and MAN in chloroform is kept at 60°C in the presence of azobisisobutyronitrile (AIBN), a white substance precipitates after about 10 min. No reaction occurs without catalyst. The polymer is soluble in acetone, dimethylformamide, dimethylsulfoxide, and insoluble in chlorinated hydrocarbons, benzene, and ether. It dissolves in boiling methanol with the formation of a polymethyl ester and in hot aqueous sodium hydroxide with the formation of a water-soluble salt of a poly-acid.

Table 1 illustrates a series of copolymerizations in which the monomer-to-monomer ratio was varied from 8/2 to 2/8. It is clear that both yield and molecular weight of the polymer are highest when equimolar amounts of both monomers were used. Figure 1 shows some time-conversion curves of the copolymerization of equimolar monomer mixtures at different temperatures. From the different rates, calculated from the maximum slopes of the curves in Fig. 1, the over-all activation energy of the copolymerization was calculated to be 17 kcal/mole. In order to determine the influence of monomer mixture composition on the copolymer composition, a series of polymerizations which were stopped at conversions lower than 5% was carried out. Figure 2 gives a survey of the results. From this figure it follows that the mole percentage of MAN units in the copolymer remains nearly constant at a value between 41 and 44% regardless of the monomer ratio.

Copolymerizations of thiophene with styrene, methyl acrylate, and acrylonitrile yielded pure sulfur-free homopolymers.

Table 1. Copolymerizations of Thiophene and MAn in Chloroform at 60°C

Mole-% thiophene in monomer mixture	Total monomer concn. (mole/liter)	Yield ^a (%)	Mole-% thiophene in copolymer	η_{red} ^b
0	5.04	5	—	—
25	5.04	64	36.7	0.13
40	5.04	74	41.9	0.14
50	5.04	74	41.5	0.15
60	5.04	53.5	42.7	0.14
75	5.04	37	43.3	0.11
100	5.04	0	—	—
50	1.26	26	42.1	—

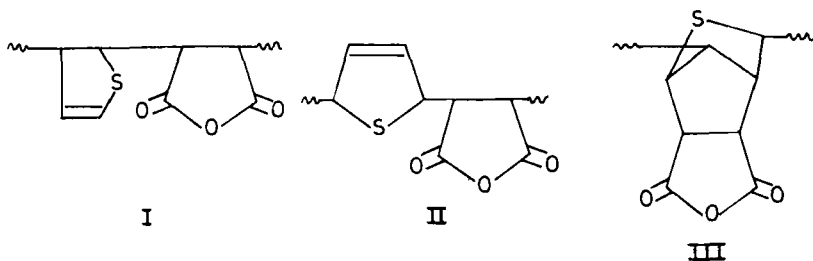
^aAfter 150 hr, [AIBN] = 0.125 mole/liter.

^bMeasured in acetone at 25°C; C = 0.50 g/dl.

Structure of the Polymer

From the nearly constant composition of the copolymers obtained from different monomer mixtures (Fig. 2), it may be concluded that they are alternating copolymers. The fact that the ratio of both comonomer units in the copolymer is not exactly 1:1 can be ascribed to different factors. Since the polymers have low molecular weights, initiator end-groups must be taken into account. Furthermore, Braun [6] showed that homopolymerization of MAn is possible. This also follows from Fig. 3, which shows that the yields obtained with high MAn concentration are higher than the maximum values that could be obtained for pure alternating copolymers. The mole fraction of MAn in the copolymers obtained in high yields is also higher than 0.5 (up to 0.63, see Table 1).

At least three different structures can be formulated for the repeating unit of the alternating copolymer:



Structure I would be formed if a normal vinyl polymerization at one of the "double bonds" of thiophene had occurred. The attack of a growing radical would occur at the β -carbon atom of thiophene which would lead to a new radical that could be stabilized by the sulfur substituent [7, 8].

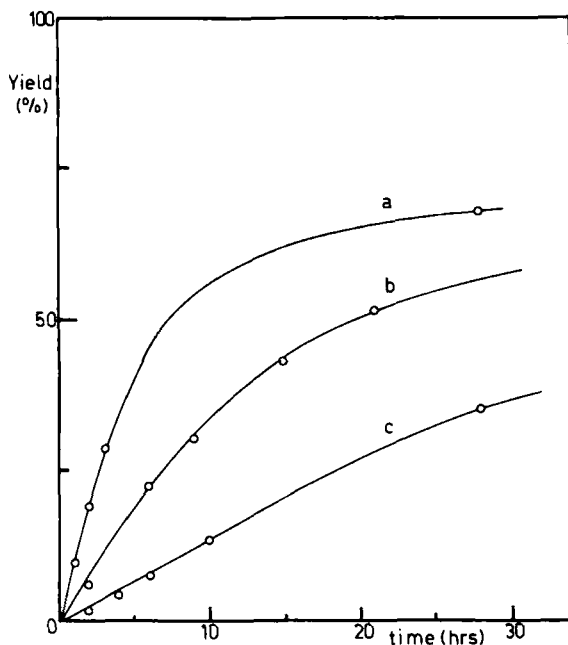


Fig. 1. Time-conversion curves of the copolymerization of equimolar amounts of thiophene and MAN in chloroform at different temperatures: (a) 70°C, (b) 60°C, and (c) 45°C. Total monomer concentration: 5 mole/liter. [AIBN]: 0.12 mole/liter.

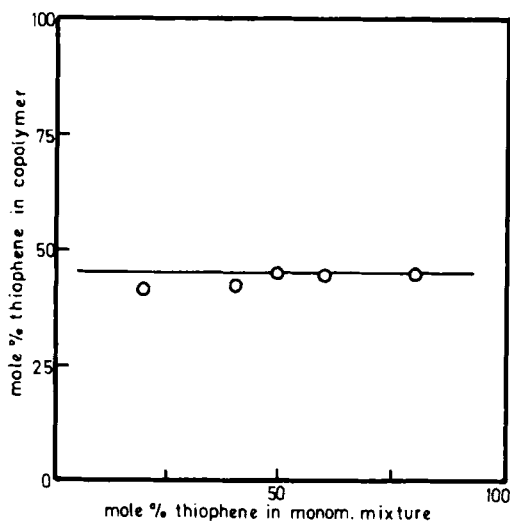
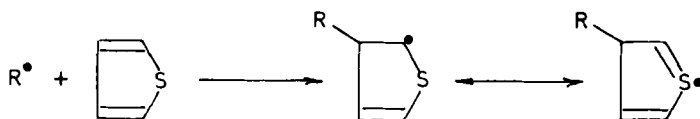
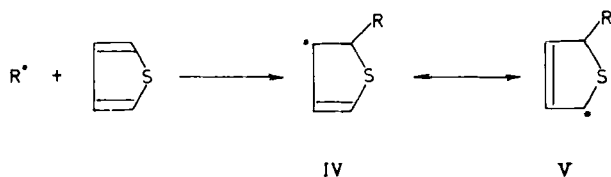


Fig. 2. Monomer-copolymer composition curve for the copolymerization of thiophene with MAN at 60°C in chloroform.



To obtain Structure II, the attack of the growing chain must occur at the α -carbon atom of thiophene. The new radical formed now would be stabilized by the presence of the double bond in the allylic position.



If IV propagates further, a repeating unit with structure I would be formed; if V propagates, Structure II would be obtained.

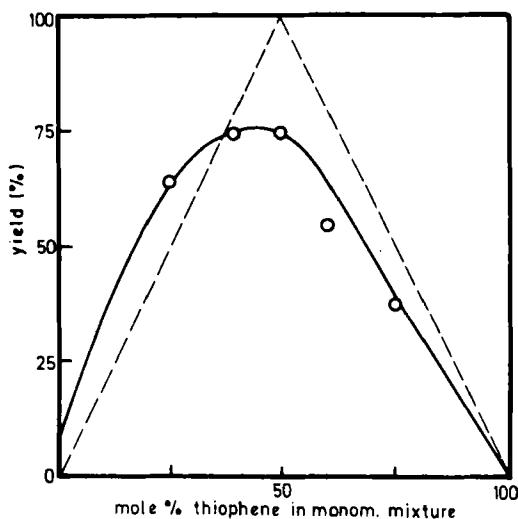
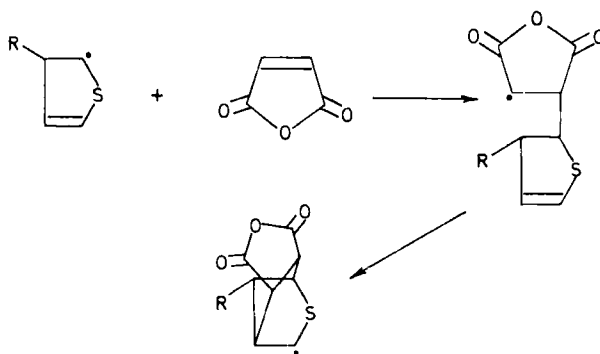


Fig. 3. Effect of the composition of the feed monomer mixture on the yield obtained after 150 hr at 60°C. The dotted lines show the maximum yields possible for pure alternating copolymers.



Structure III would be formed by a cyclocopolymerization mechanism in analogy to the copolymerization of divinyl ether with MAN described by Butler [2].

Figure 4a shows the NMR spectrum of the copolymer. The peak at δ -6 clearly demonstrates that about one double bond for each repeating unit is present. Comparison of this spectrum with the NMR spectra of 2,3-dihydrothiophene (Fig. 4b) and 2,5-dihydrothiophene (Fig. 4c) indicates that the

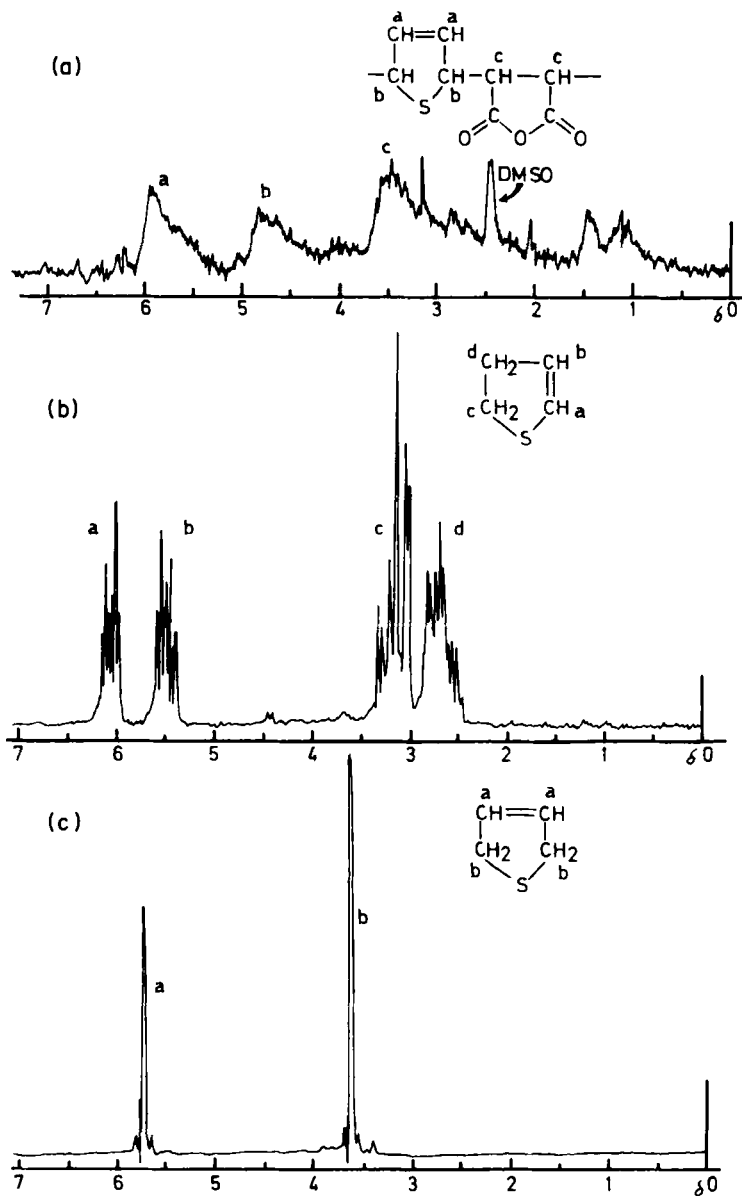


Fig. 4. (a) NMR spectrum of thiophene-MAN copolymer. (b) NMR spectrum of 2,3-dihydrothiophene. (c) NMR spectrum of 2,5-dihydrothiophene.

peak at δ -6 may be attributed to Structure II since for Structure I two peaks would be expected instead of one. Structure III would show no peak in the δ -6 region.

It may thus be concluded that the copolymer of thiophene and MAN contains no cyclopolymerized units (III) but consists mainly of Structure II. This result is analogous to the results obtained recently by Butler [9] for the copolymerization of furane with MAN.

Mechanism of Polymerization

Thiophene and MAN form a charge-transfer complex which has a K_d of 0.02 mole/liter [5]. As has been proposed for many other copolymerizations of MAN with electron-rich comonomers, the copolymerization of thiophene and MAN probably occurs via this charge-transfer complex. Further support for this hypothesis is given by the fact that the yields are lower when the monomer concentration is smaller because at lower concentration less monomer is present in complex form. The fact that the loss of about 29 kcal of resonance energy of thiophene is no obstacle for the polymerization is also an indication that both monomers polymerize via one concerted propagation step and not via two independent propagation reactions. A detailed mechanism of the propagation cannot be formulated because the exact nature of the charge-transfer complex is unknown.

EXPERIMENTAL

Polymerizations were carried out in glass vials of 10-50 ml capacity with dry chloroform as solvent. Before polymerization the vials containing the solution of monomers and catalyst were connected to a vacuum line, degassed twice, and melted off under vacuum. The vials were then transferred into a water bath thermostatted at the desired temperature. Polymers were isolated by filtration and purified by dissolving them in acetone and reprecipitating them in dry diethyl ether. Copolymer compositions were calculated from the sulfur content of the copolymers. 2,3-Dihydrothiophene and 2,5-dihydrothiophene were prepared by reduction of thiophene with sodium in liquid ammonia [10]. The two isomers were separated by preparative gas chromatography. MAN was purified by sublimation. Thiophene was distilled from calcium hydride immediately before use.

NMR spectra were recorded on the Varian 100 Mc or 60 Mc apparatus. Sulfur analyses were done by the Schöniger combustion method.

REFERENCES

- [1] T. Kokubo, S. Iwatsuki, and Y. Yamashita, *Macromolecules*, **1**, 482 (1968).
- [2] G. B. Butler and A. F. Campus, *J. Polym. Sci., Part A-1*, **8**, 545 (1970).
- [3] T. Otsu and H. Inoue, *Makromol. Chem.*, **128**, 31 (1969).
- [4] E. J. Goethals and A. Cardon, Unpublished Results (1970).
- [5] Z. Yoshida and T. Kobayashi, *Tetrahedron*, **26**, 267 (1970).
- [6] D. Braun, I. A. Aziz El Sayed, and Joannis Pamakis, *Makromol. Chem.*, **124**, 249 (1969).
- [7] C. C. Price and J. Zomlefer, *J. Amer. Chem. Soc.*, **72**, 14 (1950).
- [8] C. C. Price and H. Morita, *J. Amer. Chem. Soc.*, **75**, 4747 (1953).
- [9] G. B. Butler, J. T. Badgett, and M. Sharabash, *J. Macromol. Sci. - Chem.*, **A4**, 51 (1970); and Private Communication.
- [10] S. F. Birch and D. T. McAllan; *J. Chem. Soc.*, **1951**, 2556, 3411.

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