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NOTE

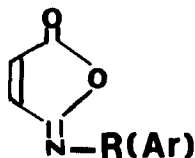
COPOLYMERIZATION OF *N*-SUBSTITUTED MALEISOIMIDES WITH VINYL ACETATE

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INTRODUCTION

N-Substituted maleisoimides have been polymerized [1, 2] and copolymerized with readily polymerizable vinylic monomers, such as acrylonitrile and vinyl acetate [3]. However, the homopolymerization or copolymerization of *N*-substituted maleisoimides is not reported in the literature. Attempts to homopolymerize *N*-substituted maleisoimides free radically have failed completely [4]. During such attempts, however, none of the maleisoimides used suffered isomerization to the corresponding imides. This paper reports the free-radical copolymerization of three *N*-substituted maleisoimides with vinyl acetate.



EXPERIMENTAL

Preparation of N-Substituted Maleisoimides. The procedure of Cotter et al. [5] was used to prepare *N*-phenyl, *N*-(*p*-bromophenyl), and *N*-benzylmaleisoimides. The compounds were purified by passing their solutions through a

column containing Fluoracil-A. *N*-Phenylmaleisoimide was further purified by recrystallization from methylene chloride at low temperature [6], while *N*-benzyl- and *N*-(*p*-bromophenyl)maleisoimides were recrystallized from 1:1 CCl₄:acetone.

Vinyl Acetate (VA). The liquid was distilled just before polymerization.

Preparation of N-Benzyl- and N-Phenylmaleimides. Literature procedures [5, 7] were used for these preparations. The *N*-benzylmaleimide was a yellow solid melting at 50°C, and the yield was 75%. IR(KBr): 1785 cm⁻¹ (imide C=O, asymmetric), 1724 cm⁻¹ (imide C=O, symmetric), 1600 cm⁻¹ (C=C). NMR: δ4.60 (s, 2H, N-CH₂-C₆H₅); δ6.85 (s, 2H, HC=CH); δ7.65 (s, 5H, C₆H₅).

Copolymerization

Copolymerization of N-Benzylmaleisoimide and VA (Copolymer I). A polymerization bottle was charged with 0.94 g (5.02 mol) *N*-benzylmaleisoimide, 20 mL CHCl₃, 0.80 g (9.29 mmol) VA, and 0.02 g AIBN. The solution was purged with nitrogen before heating at 65°C for 2.5 h. A gray precipitate which formed was filtered, washed, and dried. The softening point of the product was 185-195°C, conversion was 10%, and its intrinsic viscosity (in CHCl₃) was 0.15 dL/g. IR(KBr): 1785 cm⁻¹ (lactone C=O); 1754 cm⁻¹ (ester C=O); 1666 cm⁻¹ (-N=C); 1205 cm⁻¹, 1176 cm⁻¹ (-C-O- of isoimide and of acetate, respectively). NMR(DMSO-*d*₆): δ2.24 (s, 3H, CH₃), δ3.00-3.80 (broad, 4H, O=C-CH₂-N-CH₂-); δ7.14 (s, 5H, C₆H₅).

Copolymerization of N-Phenylmaleisoimide and VA (Copolymer II). A procedure similar to the above was employed to copolymerize these compounds, with benzene as the solvent. The copolymer did not precipitate completely with methanol, and thus the solvent was evaporated, leaving a brown viscous residue. The residue was purified by dissolving it in CHCl₃ and reprecipitating it with petroleum ether. The solidified product (5% conversion) had a softening point of 174-179°C and an intrinsic viscosity of 0.08 dL/g. IR(KBr): 1785 cm⁻¹ (imide C=O); 1724-1754 cm⁻¹ (ester and imide C=O); 1250 cm⁻¹ (-C-O- ester). NMR(CDC₃): δ1.70 (broad, 2H, -CH₂-CH); δ2.18 (s, broad, 3H, CH₃); δ3.71 (broad, 2H, O=C-CH₂-); δ5.31 (s, 1H, CH-O); δ7.42 (broad, 5H, C₆H₅); δ1.17 (broad, m, 2H, -CH₂-CH(O-COCH₃)).

Copolymerization of N-(p-Bromophenyl)maleisoimide and VA (Copolymer III). The previous procedure was used to copolymerize this isoimide with VA in pure benzene. Conversion was 6%, $[\eta] = 0.06$ dL/g, and the softening point of the pure dried copolymer was 185-189°C. IR(KBr): 1786 cm^{-1} (imide C=O); 1724-1750 cm^{-1} (ester and imide C=O). NMR(DMSO- d_6): δ 1.30 (t, broad, 2H, $-\text{CH}-\underline{\text{CH}_2}-\text{CH}-\text{O}-$); δ 2.51 (s, 3H, $\underline{\text{CH}_3}$); δ 3.35 (broad, 2H, $\text{O}=\underline{\text{C}}-\underline{\text{C}}=\text{O}$).

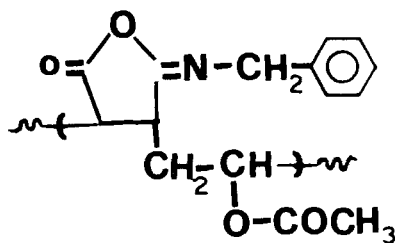


Free-Radical Copolymerization of VA With N-Phenyl- and N-(p-Bromophenyl)maleimide. These imides were copolymerized with VA in a 1:1 molar ratio according to the literature [1]. The copolymers produced were purified and dried before recording their IR and NMR spectra.

RESULTS AND DISCUSSION

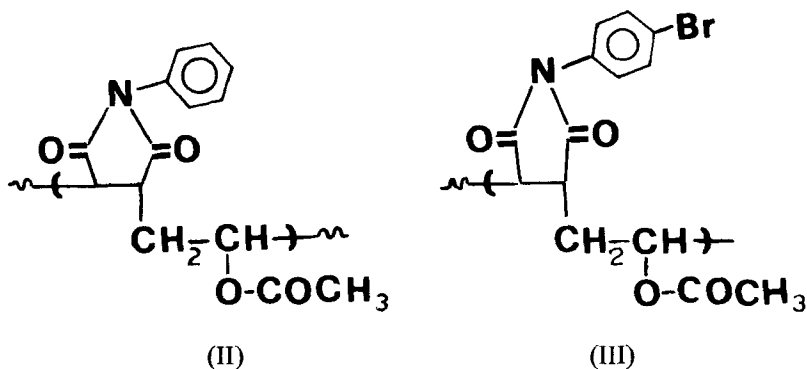
Thermally stable *N*-substituted maleisoimides were used in these studies. *N*-Phenylmaleisoimide was found stable up to 70°C, while *N*-benzyl- and *N*-(*p*-bromophenyl)maleisoimide revealed good stability upon crystallization from a CCl_4 -acetone mixture without rearrangement. The three isoimides represented *N*-alkyl and *N*-aryl derivatives for such studies. Incorporation of *N*-substituted maleisoimides into the repeating units of the three prepared copolymers was proven by chemical detection of nitrogen by the sodium fusion test, as well as by IR and NMR analysis of the products.

Spectroscopic analysis of poly(*N*-benzylmaleisoimide-*co*-VA) (I)

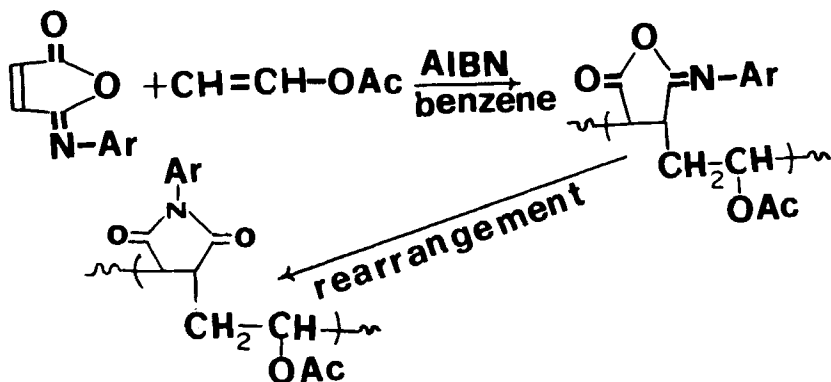


(I)

showed that *N*-benzylmaleisoimide had incorporated into the repeating unit without rearrangement to the corresponding imide. However, for poly(*N*-phenylmaleisoimide-*co*-VA) (II) and poly(*N*-*p*-bromophenylmaleisoimide-*co*-VA) (III),

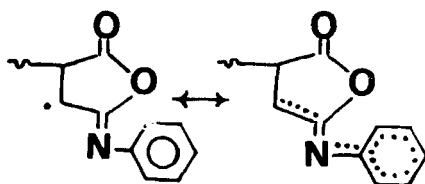


the incorporation of *N*-phenylmaleisoimide and *N*-(*p*-bromophenyl)maleisoimide were accompanied by rearrangement to the corresponding imides. Based on the thermal stabilities of the comonomers, it is very likely that the rearrangements took place after copolymerization. It had been planned to prepare the above-mentioned thermoplastic copolymers containing isoimide functional groups, and that they would hopefully rearrange gradually with time and use to the more stable structure of the corresponding imide, probably having a thermosetting property. Rearrangement of *N*-substituted isoimides to the corresponding imides is catalyzed by base [5], and perhaps sometimes by heat [8]. Model copolymers, poly(*N*-phenylmaleimide-*co*-VA) and poly(*N*-*p*-bromophenyl)maleimide-*co*-VA), prepared by free-radical polymerization, showed similar IR and NMR spectra to those obtained from copolymerization of the corresponding maleisoimides with VA.



Rearrangement of *N*-phenyl- and *N*-(*p*-bromophenyl)maleisoimide and the nonrearrangement of the *N*-benzylmaleisoimide could not be rationalized. However, it seems that *N*-alkylsuccinisoimides in the copolymer repeating units is more stable than its *N*-aryl analogs under these reaction conditions. It is also likely that the isomerization took place after conversion of the maleisoimides to the polymeric *N*-substituted succinisoimides according to the scheme at the bottom of the previous page.

With the exception of a single article [9], succinisoimides have not been reported. All attempts to prepare *N*-substituted succinisoimides have led to the formation of stable isomeric succinimides [4, 10]. The low yields and low molecular weights of the copolymers obtained may be due to the high degree of conjugation in the isoimides which would form a highly delocalized propagating radical resistant to further polymerization.



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REFERENCES

- [1] R. C. P. Cubbon, *Polymer*, 6(8), 419 (1965).
- [2] N. E. Searle, U.S. Patent 2,444,536 (1948); *Chem. Abstr.*, 42, 7340 (1948).
- [3] F. Gaetano and F. Alelio, *Chem. Abstr.*, 48, 14299a (1954).
- [4] T. M. Pyriadi, PhD Thesis, The University of Akron, Akron, Ohio, 1970.
- [5] R. J. Cotter, C. K. Saures, and J. M. Whelam, *J. Org. Chem.*, 26, 10 (1961).

- [6] T. M. Pyriadi, *J. Chem. Educ.*, **84**, 813 (1987).
- [7] M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, *Org. Synth.*, **41**, 94 (1961).
- [8] K. Hadi, MSc Thesis, University of Baghdad, Baghdad, Iraq, 1986.
- [9] C. K. Sauers, C. Marikakakis, and M. Lupton, *J. Am. Chem. Soc.*, **95**, 6792 (1973).
- [10] T. M. Pyriadi, *Bull. Coll. Sci. (U. Baghdad)*, **14**, 63 (1973); *Chem. Abstr.*, **84**, 179834j (1976).

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