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Alternating and Random Copolymers of Vinyl Acetate and Maleic Anhydride

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ABSTRACT

Alternating copolymers of vinyl acetate (VAc) and maleic anhydride (MA) are produced preferentially when VAc and MA are copolymerized at moderate temperatures while random copolymers are produced at temperatures above 90°C. A charge-transfer complex (CTC) of VAc/MA exists at moderate temperatures but does not exist at temperatures above 90°C.

INTRODUCTION

The formation of alternating copolymers from the following comonomer systems has been attributed to the presence of a charge-transfer complex (CTC) at moderate temperatures; styrene/acrylonitrile [1], α-methylstyrene/MA [2], and styrene/MA [3]. While block copolymers may be produced when a molar excess of the vinyl monomer is present at moderate temperatures [4], random copolymers are produced at elevated polymerization temperatures [5, 6].

When copolymerized at 70°C, VAc and MA yield a copolymer containing equimolar ratios of the monomers regardless of the composition of the feed [7]. That an alternating copolymer would be produced is also in accord with the reactivity ratios of VAc and MA ($r_1 = 0.055$, $r_2 = 0.003$).

The presence of a CTC for VAc/MA at moderate temperatures has been demonstrated by the use of ultraviolet (UV) and proton magnetic resonance spectroscopy (^{1}H-NMR) [8]. The absence of a CTC for VAc/MA at temperatures above 90°C has been predicted by extrapolation of UV absorbance vs temperature data.

Thus, random copolymers of VAc/MA whose compositions were dependent on the monomeric compositions were obtained when solutions of VAc and MA were heated at temperatures above 90°C in the presence of tert-butyl peroxypivalate (T-BPP). The copolymers produced were extracted by solvents and characterized by pyrolysis gas chromatography (PGC) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Solutions of mixtures of twice distilled VAc and benzene-recrystallized MA were copolymerized in the absence of oxygen and in the presence of 2.5% T-BPP by heating at specified temperatures for specific lengths of time.

^{1}H-NMR spectra were obtained for VAc, 10% solutions of MA in CCl_4, and equimolar mixtures of VAc/MA by using a Varian model T-60 instrument with tetramethylsilane as an internal standard. UV absorbance data were obtained for 10^{-4} M decalin solutions of VAc, MA, and VAc/MA by using a Carey 14 UV spectrophotometer.

PGC data were obtained by the thermal decomposition of small samples of VAc/MA polymers in a Varian Aerograph A-25 pyrolysis unit using a current of 8 amps for 6 sec. The retention times for the off gases were determined with the use of helium as the carrier gas at a flow rate of 66 ml/min in a Varian Aerograph model A100C gas chromatograph.

DSC data were obtained by use of a DuPont Model 990 thermal analyzer equipped with a DSC cell. All runs were made in a N_2 atmosphere over a temperature range of 0 to 160°C.

DISCUSSION

As shown below, the presence of the previously postulated weak CTC [9] can be shown by ^{1}H-NMR techniques. ^{1}H-NMR spectra for

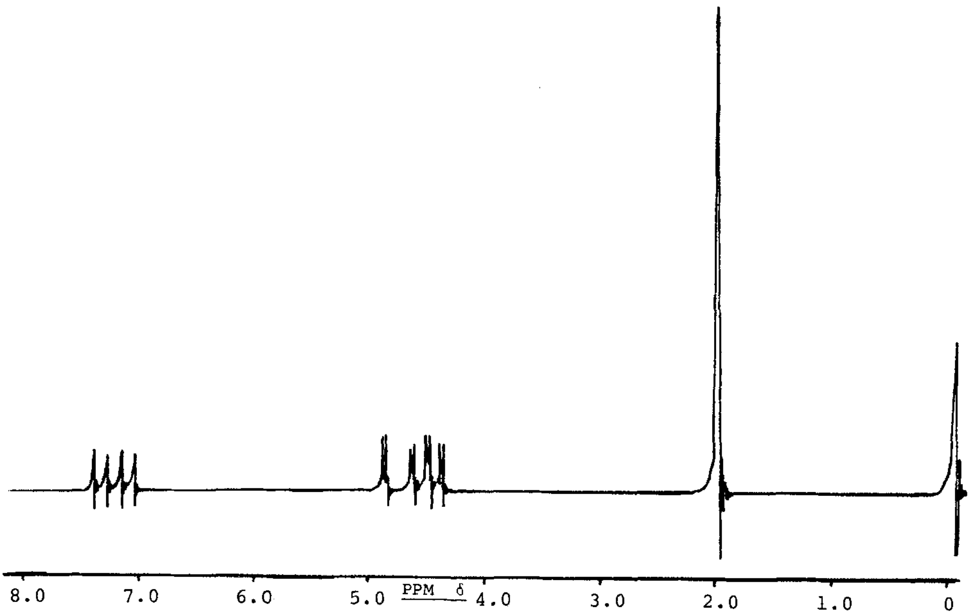
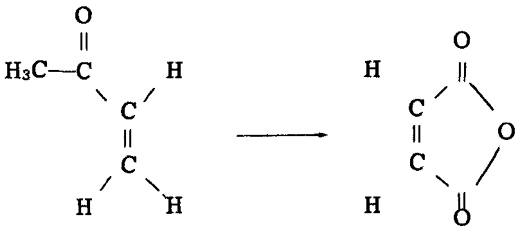


FIG. 1. Proton nuclear magnetic resonance spectrum of vinyl acetate.

VAc, MA, and VAc/MA are shown in Figs. 1-3. Small shifts from 7.24 to 7.11 δ for MA and from 4.60 to 4.56 δ for VAc are evident in Fig. 3 for an equimolar mixture of these monomers.

As shown in Fig. 4, the relative intensity of the UV absorbance band at 230 nm decreased essentially linearly as temperature increased, thus, the data may be extrapolated to zero absorbance



VAc MA

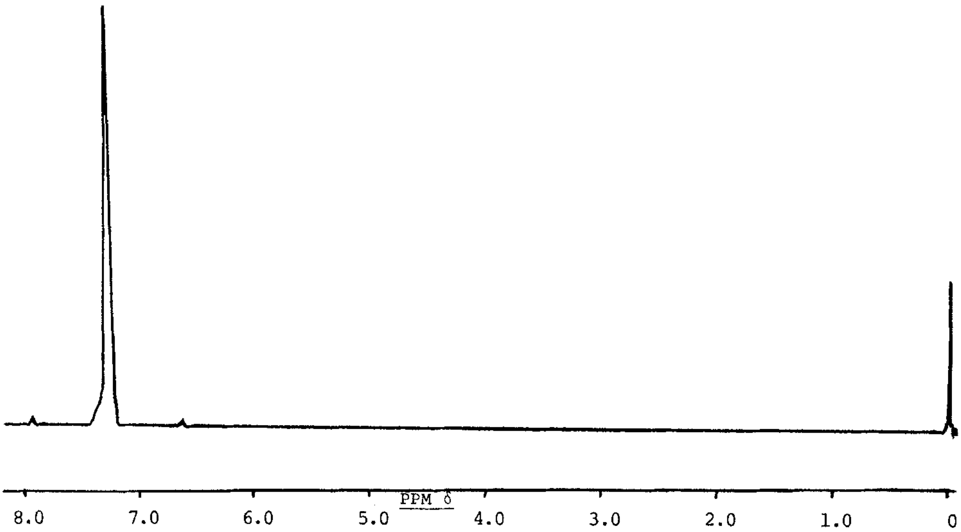


FIG. 2. Proton nuclear magnetic resonance spectrum of maleic anhydride.

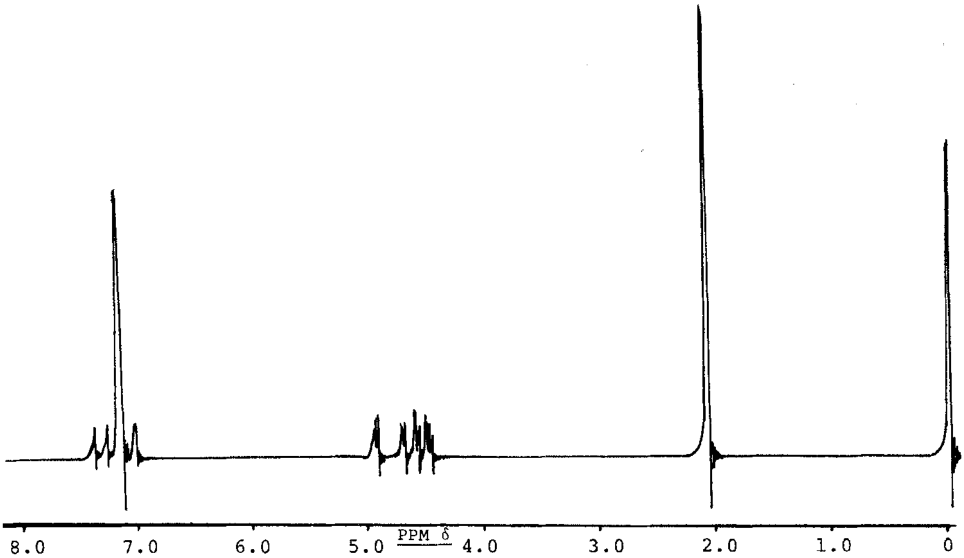


FIG. 3. Proton nuclear magnetic resonance spectrum of an equimolar solution of vinyl acetate and maleic anhydride.

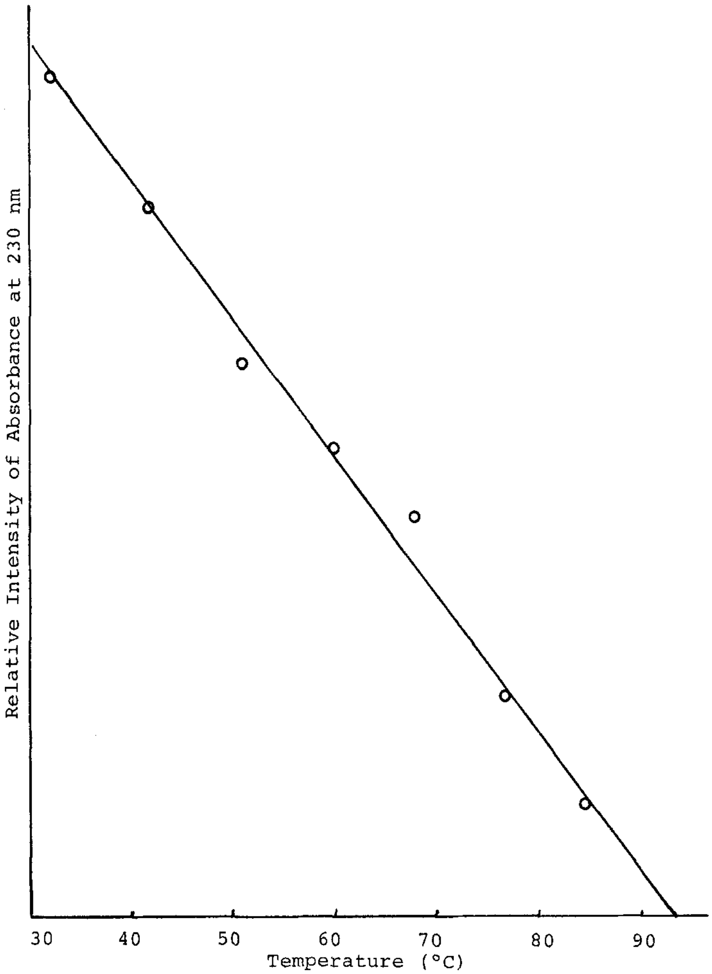


FIG. 4. Effect of temperature on the relative intensity of the UV absorbance band for CTC at 230 nm.

at a temperature slightly above 90°C. Since the CTC no longer exists, random copolymers of VAc/MA should be obtained at polymerization temperatures above 90°C.

PGC data for typical polyVAc (PVAc), alternating copolymer of VAc/MA obtained in good yield at 80°C, and a random copolymer of VAc [5] and MA [1] obtained in good yield at 100°C are shown in parts A, B, and C of Fig. 5, respectively. Since the thermal decomposition

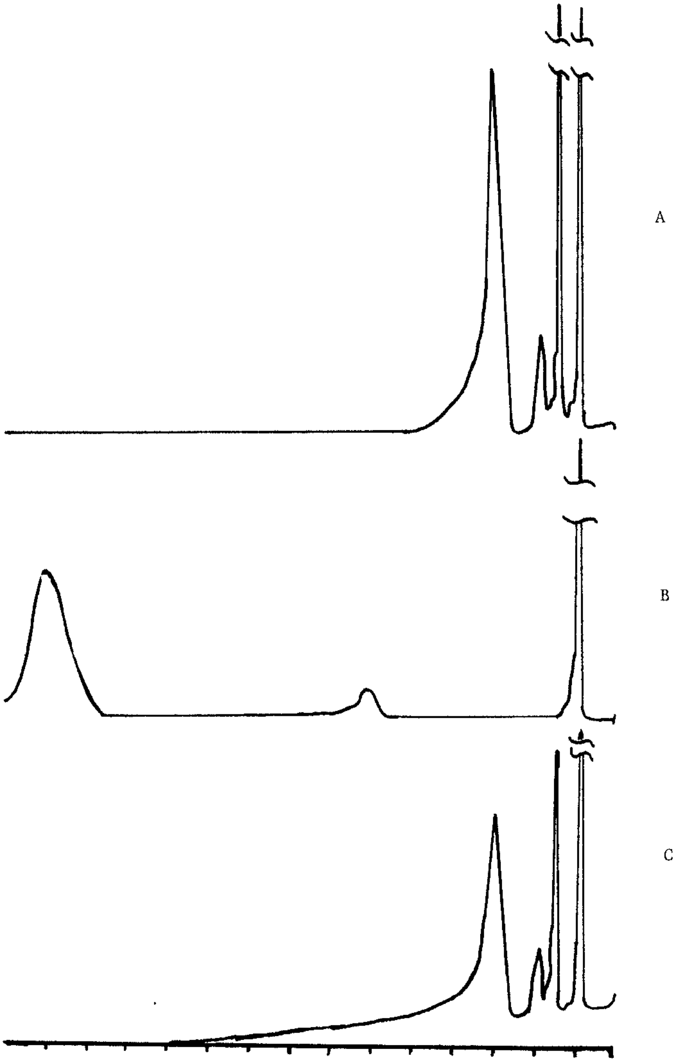


FIG. 5. Typical PGC pyrogram of (A) PVAc, (B) VAc/MA, and (C) VAc/MA random copolymer.

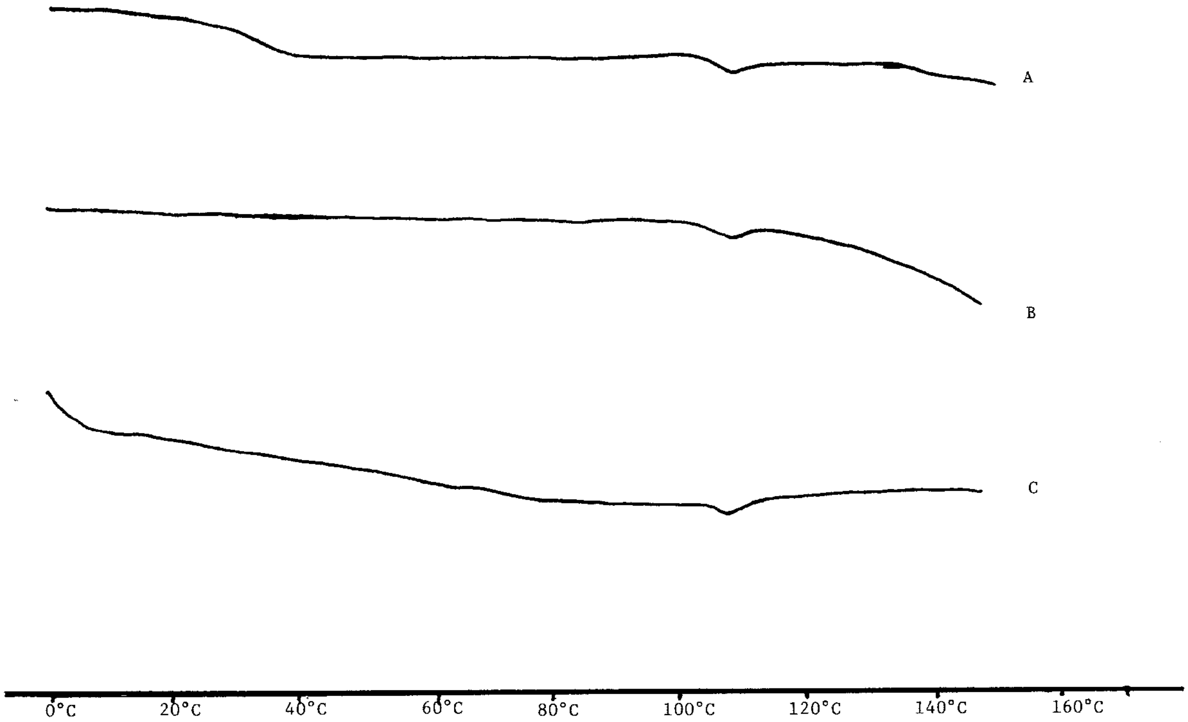


FIG. 6. Typical DSC thermograms of (A) PVAc, (B) VAc/MA alternating copolymer, and (C) VAc/MA random copolymer.

mechanism for VAc polymers and copolymers depend on the sequential distribution of VAc in the polymer chain, quantitative PGC data are not obtainable. However, the PGC data are characteristic and the pyrogram of the random copolymer is very much different than that of the alternating copolymer.

Likewise, the DSC thermogram for PVAc, alternating copolymer of VAc/MA and the random copolymer of VAc/MA shown in parts A, B, and C, respectively, of Fig. 6 are characteristically different. The typical T_g for PVAc at about 30°C shown in Fig. 6A is not evident in Fig. 6B for the alternating copolymer of VAc/MA. While this typical T_g is also not evident in Fig. 6C, the thermogram has a characteristic negative slope in the range of 20-80°C.

CONCLUSIONS

The CTC of VAc/MA which is detected by UV and ^{1}H-NMR spectroscopy is shown to be nonexistent at temperatures above 90°C. Yields of over 90% based on monomers present, show that most of the reactants were converted to polymeric products. Hence, it may be concluded that alternating copolymer and random copolymers of VAc/MA are produced at temperatures below 90°C and at higher temperatures, respectively.

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REFERENCES

[1] N. G. Gaylord and G. Takahashi, Adv. Chem. Ser., 91, 94 (1969).
[2] R. B. Seymour and D. P. Garner, Polymer, 17, 21 (1976).
[3] R. B. Seymour and D. P. Garner, J. Coatings Technol., 48, 41 (1976).
[4] R. B. Seymour, P. D. Kincaid, and D. R. Owen, Adv. Chem. Ser., 129, 230 (1973).
[5] I. E. Muskat, U. S. Pat. 3,388,106 (June 1, 1968).
[6] R. B. Seymour, D. P. Garner, G. A. Stahl, R. Knapp, and L. J. Sanders, Polymer 1977, 18, 1157.

[7] G. Smets and M. C. deWilde, J. Polym. Sci., 5, 253 (1950).
[8] C. Caze and C. Locheux, J. Macromol. Sci. A9, 29 (1975).
[9] C. Caze and C. Locheux, J. Macromol. Sci. A7, 991 (1973).

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