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## Free-Radical Copolymerizations of N-Phenyl Maleimide

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### ABSTRACT

Free radical-initiated copolymerization of N-phenyl maleimide (NPMI) with styrene (St), vinyl acetate (VAc) and methyl methacrylate (MMA) at 35° C in benzene solution initiated by AIBN was studied. The copolymerization of NPMI and St yields a "nearly equimolecular" alternating copolymer, irrespective of monomer feed. Reactivity ratios of NPMI with St, VAc, and MMA were determined by a curve-fitting method which has the advantage of delivering values not involving personal judgement.  $Q_1$  and  $e_1$  values of NPMI were also calculated. Tentative explanations have been proposed to interpret the "nearly alternating" copolymerization between NPMI and St. In addition, thermal stabilities of copolymers were studied by using a programmed thermogravimetric analysis technique. Copolymers of St, VAc, and MMA show a considerable increase in thermal stability with increasing content of NPMI. The glass transition temperatures of copolymers of NPMI with MMA and St were measured by differential scanning calorimetry. In both series of copolymers the glass transition

temperature increases markedly with increasing in NPMI content. In the case of NPMI-St copolymers, the relative thermal stability as well as glass transition temperature also corroborated the nearly alternating behavior observed.

## INTRODUCTION

At the present there is considerable interest not only in synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications under unusual working conditions. In general, we have at our disposal a great number of macromolecular compounds, but some of them are classical from different points of view; however, very often they cannot be used under unusual working conditions because they do not possess suitable properties. One of the existing methods to improve such properties consists in the preparation of copolymers of different compositions by varying the nature and relative amount of the two monomer units in the copolymer.

A knowledge of the copolymerization process is therefore of considerable interest, since it provides information on the reactivity of several growing species towards a monomer, as well as the reactivity ratios of a series of monomers against a reference radical.

For the present study three monomers, styrene, vinyl acetate, and methyl methacrylate, have been selected because of their wide use in the field of the modern plastics technology. The goal of this study is assessment of these monomers in possible copolymerization with a monomer such as the N-phenyl maleimide, whose incorporation into the backbone chain could present a considerable and promising interest. Since the latter is a monomer with a structure of the 1,2-ethylenic type, that at the same time is a five-membered planar ring which completely hinders the rotation of the imide residues around the backbone chain of the macromolecule, it must lead to copolymers with a great structural stiffness as well as a higher thermal stability.

The main objectives of the present study are three principal aspects, which are intimately related: first, to determine the reactivity ratios from the composition diagram by means of a pre-established model following one of the existing procedures; secondly, to assess the influence of the copolymer composition on the thermal stability by using a thermogravimetric analysis technique (TGA); finally, to establish the dependence of the glass transition temperature ( $T_g$ ) on the copolymer composition by means of differential scanning calorimetry (DSC).

Data concerning the copolymerization of N-phenyl maleimide are

very scarce; only very recently has its copolymerization with vinyl chloride [1] and methyl methacrylate [2] been reported.

Braun et al. [3], following Tidwell and Mortimer [4], classified the determination of the reactivity ratios into four groups: (a) approximation, (b) curve-fitting, (c) intersection [5], and (d) linearization [6] methods. In the curve-fitting method proposed by Alfrey et al. [7], the reactivity ratios are estimated by trial and error approximation; therefore the method involves some personal judgement. The procedure proposed by Braun et al. [3] is a curve-fitting method having the advantage of not requiring an estimation of the  $r$  values in advance. This method has been used through all the work.

## EXPERIMENTAL

### Monomers, Initiator, and Solvent

#### N-Phenyl Maleimide (NPMI)

The synthesis of NPMI was carried out in two stages according to the original method developed by Searle [8]. To 98 g (1 mole) of maleic anhydride (Carlo Erba, Milan) in 230 ml of chloroform (Carlo Erba, Milan) 93 g (1 mole) of freshly distilled aniline (Probus, S.A.) dissolved in 125 ml of chloroform was added slowly dropwise with vigorous stirring. The temperature was kept constant between 16 and 18° C. The resulting product, a fine precipitate, was filtered, washed with chloroform and dried in a vacuum oven at 40° C for 24 hr, giving 182.2 g (95.3% yield). It was recrystallized from ethyl alcohol (Ferosa S.A.), giving hexagonal lamellar crystals with a mp 202° C, in complete agreement with that given by Searle [8] and Ivanov et al. [9].

Analysis. Calcd for  $C_{10}H_9O_3N$  (191): C, 62.62%; H, 4.74%; N, 7.32%. Found: C, 62.61%; H, 4.74%; N, 7.40%. IR spectrum (KBr), 3275, 3100, 1695, 1620, 1585, 1540, 1490, 975, 855, and 760  $cm^{-1}$ . NMR spectrum ( $\tau$ ),  $(CD_3)_2SO$ , 3.60 quartet (2H,  $-CH=CH-$ ), 2.55 multiplet (5H, aromatics), -0.45 singlet (1H,  $-CONH-$ ), -2.90 (1H,  $-COOH$ ).

In the second stage, 144.5 g (0.76 mole) of the above compound was treated with 38.5 g of anhydrous sodium acetate and 385.5 g (3.78 mole) of 95% acetic anhydride, giving 122.8 g (93.8%) yield; after recrystallization from ethyl alcohol-water (1:2) this product gave rectangular prismatic crystals, mp 90° C, in complete agreement with literature data [8-10].

Analysis. Calcd for  $C_{10}H_7O_2N$  (173): C, 69.35%; H, 4.07%; N,

8.08%. Found: C, 69.30%; H, 4.01%; N, 8.25%. IR spectrum (KBr), 3100, 1770, 1705, 1600, 1505, 1390, 1150, 840, 760, and 700  $\text{cm}^{-1}$ . NMR spectrum ( $\tau$ ),  $\text{CCl}_3\text{D}$ , 3.30 singlet (2H,  $-\text{CH}=\text{CH}-$ ), 2.70 singlet (5H, aromatics).  $R_f = 0.37$  on silica gel plate 60 PF<sub>254</sub> (Merck A.G.), benzene-ethyl acetate (80:20) as eluent, ultraviolet lamp (254 and 350 nm) as developer.

### Styrene

A 150-ml portion of a commercial reagent styrene (Fluka A.G.) was washed three times with 5% (100 ml) sodium thiosulfate, twice with 10% solution (100 ml) of sodium hydroxide (Panreac S.A.) to eliminate inhibitor, and a few times with distilled water and then dried overnight over anhydrous calcium chloride (Quimipur S.A.). Styrene dried in this manner was distilled at reduced pressure over anhydrous calcium hydride and under a nitrogen atmosphere, abundant head and tail cuttings being discarded. The middle cut of the above product was distilled again over calcium hydride in a vacuum line when required.

### Methyl Methacrylate

A 150-ml portion of an extra pure grade reagent methyl methacrylate (Merck A.G.) was washed three times with 5% (100 ml) sodium thiosulfate and twice with a 10% solution (100 ml) of sodium hydroxide to eliminate inhibitor (hydroquinone). It was dried on a vacuum line over anhydrous calcium hydride, head and tail fractions being discarded.

### Vinyl Acetate

Vinyl acetate (Hoechst A.G.) was purified, after the inhibitor has been removed by distillation according to ordinary methods. The middle cut of the distillate was distilled again in vacuum over anhydrous calcium hydride just before use.

The purity of all three monomers was determined by GLC and found to be greater than 99.9%.

### Initiator

The initiator, 2,2'-azobisisobutyronitrile (AIBN) (Fluka A.G.) was purified by fractional crystallization by a two-stage procedure previously described in detail [ 11] from methyl alcohol four times and then dried and stored in a dark, cool place. Its melting point was determined with a Perkin-Elmer DSC-1B differential scanning calorimeter and found to be  $104 \pm 1^\circ \text{C}$ .

### Solvent

Benzene was purified by appropriate chemical methods [ 12], then distilled over sodium wire in a 150-cm column packed with glass rings and with an automatic collector. Immediately prior to use it was twice vacuum-distilled over anhydrous calcium hydride before being introduced into glass ampoules.

### Copolymerization Technique

All the glass material employed was washed before use with dilute permanganic acid solution, hydrogen peroxide acid solution, distilled water, and finally dried in a vacuum oven at 120° C for 24 hr.

Polymerization ampoules of Pyrex glass were charged by means of a transfer technique. Given amounts of N-phenyl maleimide and AIBN were sealed off and maintained under vacuum for 5 hr at room temperature attached to a high vacuum line at  $10^{-5}$  Torr. In the second stage, the comonomers (St, VAc, or MMA) were put into the ampoules after repeated freeze-and-thaw cycles with liquid nitrogen. Polymerization was carried in a water bath which was thermostatted at  $35 \pm 0.1^\circ$  C. Polymerizations were stopped by opening the glass ampoules and immediately pouring the contents into a large amount of methyl alcohol (NPMI-St and NPMI-MMA copolymers) or ethyl alcohol (NPMI-VAc copolymers). The materials precipitated from methyl alcohol or ethyl alcohol solutions were washed repeatedly with a large amount of hot methanol or ethanol and dried under vacuum at 50° C until constant weight was attained.

### Copolymer Analysis

Copolymer compositions were calculated on the basis of the nitrogen contents of the copolymers, determined by using a Perkin-Elmer elemental analyzer, Model 240. The polymerization conditions, the compositions, intrinsic viscosity, and other characteristic parameters for copolymers are shown in Tables 1, 2, and 3. The relationships between  $f_1$ , the initial molar fractions of NPMI in the monomer feed, and  $F_1$ , the molar fractions of NPMI in the copolymers are shown in Figs. 1 and 2. The monomer reactivity ratios  $r_1$  and  $r_2$  were calculated according to the curve-fitting method of Braun et al. [ 3]. The  $r_1$  and  $r_2$  values obtained are summarized in Table 4. In Figs. 1 and 2, the polymerization curves obtained from these  $r_1$  and  $r_2$  values are shown as solid lines.

TABLE 1. Copolymerization of NPMI ( $M_1$ ) and St ( $M_2$ ) in Benzene at 35° C with AIBN as Initiator, (Polymerization Times 30-100 min)

| $f_1$ | Yield (%) | N (%) | $F_1$ | $[\eta]$ (ml/g) | $T_i$ (°C) | $T_g$ (°C) |
|-------|-----------|-------|-------|-----------------|------------|------------|
| 0.05  | 3.10      | 4.66  | 0.449 |                 | 329        |            |
| 0.10  | 3.60      | 4.77  | 0.463 | 250.0           | 334        | 225        |
| 0.20  | 5.00      | 4.98  | 0.492 | 172.0           | 343        | 230        |
| 0.30  | 9.83      | 4.86  | 0.475 | 265.0           | 343        |            |
| 0.30  | 3.25      | 4.98  | 0.490 |                 | 329        |            |
| 0.39  | 2.46      | 5.34  | 0.538 |                 | 357        |            |
| 0.39  | 23.38     | 5.02  | 0.495 | 308.0           | 348        | 229        |
| 0.50  | 9.10      | 5.07  | 0.502 | 237.0           | 348        | 235        |
| 0.60  | 9.40      | 5.18  | 0.517 | 183.0           | 353        | 233        |
| 0.68  | 19.40     | 5.29  | 0.531 | 101.2           | 357        | 234        |
| 0.80  | 13.00     | 5.51  | 0.562 |                 | 362        | 238        |
| 0.90  | 11.20     | 5.50  | 0.561 | 92.9            | 363        | 247        |

TABLE 2. Copolymerization of NPMI ( $M_1$ ) and VAc ( $M_2$ ) in Benzene at 35° C with AIBN as Initiator (Polymerization Times 4-14 hr)

| $f_1$ | Yield (%) | N (%) | $F_1$ | $[\eta]$ (ml/g) | $T_i$ (°C) |
|-------|-----------|-------|-------|-----------------|------------|
| 0.11  | 3.68      | 5.67  | 0.538 | 18.5            | 217        |
| 0.20  | 5.37      | 5.88  | 0.570 | 26.0            | 246        |
| 0.30  | 9.57      | 6.30  | 0.636 | 19.5            | 236        |
| 0.40  | 3.90      | 6.57  | 0.683 | 20.2            | 241        |
| 0.48  | 14.41     | 6.77  | 0.717 | 41.2            | 246        |
| 0.59  | 2.95      | 6.89  | 0.740 | 26.5            | 261        |
| 0.70  | 5.58      | 7.20  | 0.801 | 23.6            | 266        |
| 0.82  | 3.16      | 7.54  | 0.870 | 19.0            | 305        |
| 0.89  | 4.92      | 7.74  | 0.916 | 20.0            | 340        |

TABLE 3. Copolymerization of NPMI ( $M_1$ ) and MMA ( $M_2$ ) in Benzene at 35°C with AIBN as Initiator (Polymerization Times 2-3 hr)

| $f_1$ | Yield (%) | N (%) | $F_1$ | $[\eta]$ (ml/g) | $T_i$ (°C) | $T_g$ (°C) |
|-------|-----------|-------|-------|-----------------|------------|------------|
| 0.10  | 3.83      | 1.11  | 0.084 | 55.4            | 256        |            |
| 0.18  | 5.02      | 1.96  | 0.156 | 44.4            | 275        | 143        |
| 0.29  | 4.85      | 2.82  | 0.242 | 59.0            | 305        | 158        |
| 0.40  | 4.75      | 3.46  | 0.302 | 51.0            | 329        | 171        |
| 0.47  | 7.53      | 3.88  | 0.348 | 62.9            | 338        | 179        |
| 0.58  | 6.51      | 4.67  | 0.441 | 94.6            | 343        | 189        |
| 0.73  | 5.14      | 5.00  | 0.484 | 37.0            | 353        | 199        |
| 0.76  | 3.92      | 5.88  | 0.606 | 35.3            | 357        | 213        |
| 0.89  | 2.23      | 6.26  | 0.664 |                 | 357        |            |
| 0.90  | 3.66      | 6.21  | 0.656 | 39.1            | 367        | 221        |

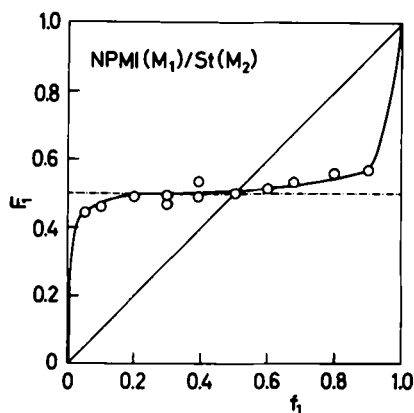


FIG. 1. Diagram for radical copolymerization of N-phenyl maleimide ( $M_1$ ) with styrene ( $M_2$ ) in benzene at 35°C with AIBN as initiator: (—) curve drawn by using the reactivity ratios values obtained according to a curve-fitting method by adoption of a nonlinear mean-square procedure,  $r_1 = 0.047$  and  $r_2 = 0.012$  as shown in Table 4; (· - ·) equimolar composition of an alternating 1:1 copolymer.



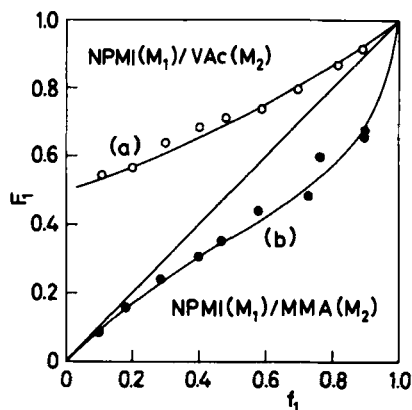


FIG. 2. Diagrams for radical copolymerization of (a) N-phenyl maleimide ( $M_1$ )-vinyl acetate ( $M_2$ ) and (b) N-phenyl maleimide ( $M_1$ )-methyl methacrylate ( $M_2$ ) in benzene at 35°C with AIBN as initiator. Curves drawn by using the reactivity ratios values obtained according to a curve-fitting method by adoption of a non-linear mean-square procedure: (a)  $r_1 = 1.269$ ,  $r_2 = 0.00$ ; (b)  $r_1 = 0.183$ ,  $r_2 = 1.022$ , as shown in Table 4.

TABLE 4.  $Q$  and  $e$  Values of the Alfrey-Price Equation for the Free-Radical-Initiated Copolymerization of N-Phenyl Maleimide ( $M_1$ )

| $M_2$               | $r_1$ | $r_2$ | $Q_2$<br>[44] | $e_2$<br>[44] | $Q_1$ | $e_1$ | Reference  |
|---------------------|-------|-------|---------------|---------------|-------|-------|------------|
| Styrene             | 0.047 | 0.012 | 1.00          | -0.80         | 9.35  | 1.94  | This paper |
| Vinyl acetate       | 1.269 | 0.00  | 0.026         | -0.22         |       |       | This paper |
|                     | 0.66  | 0.02  |               |               | 0.74  | 1.75  | [43]       |
| Methyl methacrylate | 0.183 | 1.022 | 0.74          | 0.40          | 1.26  | 1.69  | This paper |
|                     | 0.30  | 0.98  |               |               | 1.18  | 1.51  | [45]       |
|                     | 0.15  | 0.90  |               |               |       |       | [2]        |
| Vinyl chloride      | 0.03  | 3.82  | 0.044         | 0.20          | 0.02  | 1.67  | [1]        |

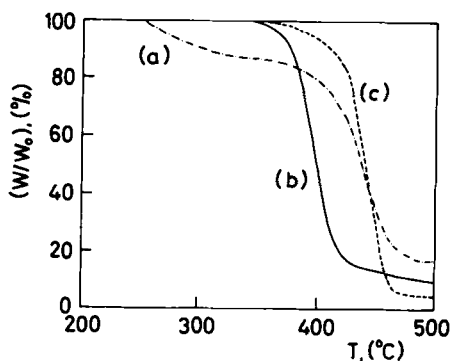


FIG. 3. Thermogravimetric analysis diagrams ( $10^{\circ}\text{C}/\text{min}$ ): (a) N-phenyl maleimide ( $M_1$ )-vinyl acetate ( $M_2$ ),  $F_1 = 0.570$  and  $T_i = 246^{\circ}\text{C}$ ; (b) N-phenyl maleimide ( $M_1$ )-methyl methacrylate ( $M_2$ ),  $F_1 = 0.441$  and  $T_i = 343^{\circ}\text{C}$ ; (c) N-phenyl maleimide ( $M_1$ )-styrene ( $M_2$ ),  $F_1 = 0.517$  and  $T_i = 353^{\circ}\text{C}$ .

### Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out by means of a Du Pont 950 apparatus which has a Du Pont 900 as a control unit. Experimental working conditions and other details have been carefully described previously [13, 14]. Samples were dried in a high vacuum drying oven at  $60^{\circ}\text{C}$  for 24 hr. The thermal stability of the copolymer has been arbitrarily defined as a function of the initial weight loss and the temperature by specifying as particular environmental conditions a  $10^{\circ}\text{C}/\text{min}$  heating rate and an  $\text{N}_2$  atmosphere ( $A_228$ , SEO S.A.) at a flow rate of 10 ml/sec. Experimental results are given in Tables 1-3. For purposes of comparison three thermograms on the studied series of copolymers are shown in Fig. 3.

### Differential Scanning Calorimetry (DSC)

Glass transition temperatures  $T_g$  of the copolymers in the solid state have been measured with a differential scanning Perkin-Elmer,

Model DSC-1B calorimeter, which was calibrated with standards such as: highly purified metals, zinc, lead, indium and tin (Perkin-Elmer, Connecticut), phenacetin, acetanilide, benzil, and azobenzene (Reichert, Vienna). Melting points of all the compounds were taken from literature data [15, 16]. Measurements as well as the calibration were carried out at a heating rate of 8°C/min. For the determination of  $T_g$  from the DSC traces, a criterion suggested by Shultz and Gendron [17] was adopted:  $T_{1/2}$  was taken as the temperature at the mid-point of the line drawn between  $T_u$  and  $T_w$ ,  $T_u$  and  $T_w$  being the temperatures of intersection of the initial and final tangents, respectively, with the tangent drawn through the inflection point  $T_u$  of the DSC curve. A good precedent for this criterion exists from a practical point of view [18], and there are good theoretical arguments for it [19]. The experimental data are summarized in Tables 1 and 3. The glass transition temperature for NPMI-VAc copolymers lies close to  $T_i$ . Its determination was extremely difficult.

### Viscometry

Intrinsic viscosities were measured with a suspended level Ubbelohde-type dilution viscometer in N,N-dimethylformamide at 30°C. The intrinsic viscosities were calculated by means of Huggins' equation [20].

### Spectroscopic Measurements

The NMR spectra of NPMI were measured in  $CCl_4$ , benzene, and styrene solutions, tetramethylsilane (0.5%) being used as an internal standard. Dilute solutions (5% w/v) of NPMI were used to eliminate the chemical shift contribution to solute-solute interactions. Measurements of the spectra were carried out at 37°C with a 60 MHz Perkin-Elmer Model R-10 spectrometer.

In order to determine the existence of the charge-transfer complexes between NPMI and St, the UVI light spectra were obtained by using a Perkin-Elmer Model 403 spectrophotometer with quartz cell of 1 cm path length at room temperature. A continuous variation method [21] was used. Benzene and cyclohexane (Uvasol spectro-quality, Merck A.G.) were used as solvents.

## RESULTS AND DISCUSSION

Three well defined types of copolymerization behavior have been found in the present work. The curve in Fig. 1 illustrates a characteristic copolymerization for the system NPMI ( $M_1$ )/St ( $M_2$ ) with a tendency toward alternation. Table 1 shows that varying the molar ratios of monomers changes the copolymer composition of 1:1 alternate units appreciably. The same type of alternation can be noticed in the copolymerization of styrene with N-butyl maleimide [22], N-maleimide [23], N-bornyl maleimide [24], N-(p-chlorophenyl) maleimide [25], N-(carboxy p-phenyl) maleimide [25], and other N-maleimides, and maleic anhydride [26].

Since a "nearly alternating" copolymerization behavior between St and NPMI has been found, in order to clarify some aspects of the process it was necessary to explore the features of conventional alternating copolymerization. For instance, many examples of alternating copolymerization in the case of maleic anhydride (MAH) have been reported in the literature by several authors [29]. Now, it is generally accepted that this type of polymerization implies the participation of a charge-transfer complex between both comonomers. Two types of mechanism have been proposed [27]: (a) homopolymerization of the charge-transfer complex [28] and (b) a mechanism involving both free monomers and the charge-transfer complex [29-31].

Monomers producing alternating copolymers in the conventional sense of free-radical polymerization are classified as specific acceptor monomers presenting large  $e$  values in combination with electron-donor monomers [32]. Typical examples of acceptor monomers can be maleic anhydride and N-maleimide; and a typical electron donor is styrene.

Charge-transfer complexes of monomers, such as maleic anhydride and styrene, have been detected and their equilibrium constants were measured by Tsuchida and Tomono [29] by studying their ultraviolet and visible spectra (UVI) and nuclear magnetic resonance spectra (NMR). In this paper it was necessary to carry out a study of the effect of possible participation of the charge-transfer complex on the "nearly alternating" copolymerization between NPMI and St.

The existence of the complex can be deduced by analyzing some changes in the absorption spectra of mixtures of the two monomers in comparison with the spectrum of each of the components. Therefore, in order to determine the existence of charge-transfer complexes between NPMI and St with benzene as solvent (which usually acts as an electron-donor interacting relatively weakly with acceptor monomer), UVI spectra were recorded. NPMI/St mixtures of

varying composition were examined by a continuous variation method [21]. Neither appreciable change of color upon mixing these components nor the appearance of new independent bands was observed irrespective of the pure monomers.

On the other hand, we explored the formation of charge-transfer complexes in an inactive solvent such as cyclohexane to eliminate the solvent influence on the monomers complexation. Our UVI results suggest that NPMI and St are not complexed in cyclohexane, since we did not detect any appreciable charge-transfer bands. We measured monomer bands in the near UVI region (273.5, 282.5, 291, and 323 nm) by calculating the apparent absorbance observed and those of NPMI and St calculated from separate runs. The results suggest the possibility that both monomers are completely uncomplexed if they are diluted with cyclohexane.

However there are some data in the literature regarding the existence of complexes without charge-transfer bands independently of their component molecules [28]. In such cases, the thin-film procedure as proposed by Bryce-Smith et al. [33] must be used, since charge-transfer bands are located uncomfortably close to the absorption edges of those appearing in aromatic compounds. Despite the presence of benzene we have phenyl groups located in both NPMI and St monomers. Hence, according to the above results it is not possible to probe the true existence of charge-transfer complexes.

Hanna and Ashbaugh [34] and Carter [35] have proposed NMR spectroscopy as a tool for studying the existence of undetectable UVI weak complexes. Bryce-Smith and Hems [36] found, by means of NMR chemical shifts of the ethylenic protons of maleic anhydride, NPMI, and other N-substituted maleimides in benzene and in  $\text{CCl}_4$  solution, that large upfield chemical shifts are induced by the benzene solvent; these are attributed to a 1:1 exo-stereospecific association of the solute and solvent molecules. Moreover, the larger value of the increment of chemical shifts found with maleic anhydride may imply that other factors, such as solute size and the fact that carbonyl groups of acid anhydride have a larger double bond character than those of the corresponding imide and therefore a larger acceptor character, as indicated by Matsuo [37], permit a closer approximation of maleic anhydride to the benzene ring. Furthermore, as Matsuo has also shown [37], there exist no appreciable differences between chemical shift for N-ethyl maleimide and N-ethyl succinimide, and little differences between maleic anhydride and succinic anhydride.

The main conclusions, according to Matsuo [37], for the specific interactions we are considering, are due primarily to the nature of the carbonyl groups. From this point of view the double bonds of the solute play only minor role. In our NMR spectra, characteristic

chemical shifts of the olefinic protons of NPMI appeared at  $\delta(\text{CCl}_4)$ , 407 cps;  $\delta(\text{C}_6\text{H}_6)$ , 352.5 cps;  $\delta(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5)$ , 356 cps. The solvent-induced chemical shifts are  $\Delta = \delta(\text{CCl}_4) - \delta(\text{C}_6\text{H}_6) = 54.5$  cps and  $\Delta = \delta(\text{CCl}_4) - \delta(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5) = 51.0$ . From this can be seen that the values for benzene and St show no appreciable difference, suggesting that both ethylenic protons on the NPMI molecule should be located where the magnetic anisotropic effect of the phenyl nucleus of styrene can be easily and strongly accepted [38], similarly as proposed in the case of the MAh-St system [39].

In the case of NPMI-VAc copolymerization, the monomer reactivity ratio for NPMI is much larger than the other. In this case,  $r_1 = 1.269 \gg r_2 = 0.00$ , both types of propagating species add NPMI preferentially. There is a tendency toward consecutive homopolymerization. NPMI tends to homopolymerize until it is consumed [40]. In the NPMI-VAc system, NPMI radical, which is stabilized by  $>\text{C}=\text{O}$ , is less reactive than the vinyl acetate one radical. On the contrary, NPMI monomer is much more reactive than vinyl acetate monomer, since it has a higher tendency to produce stabilized radicals. In other words, the order of substituents for enhancing radical reactivity is opposite to their order for enhancing monomer reactivity. Moreover, the radical  $\text{M}_1^*$ , less reactive, will preferentially add  $\text{M}_1$  at a much greater rate than monomer  $\text{M}_2$ . Equally,  $\text{M}_2^*$ , which is more reactive, will preferentially add  $\text{M}_1$  at a greater rate than  $\text{M}_2$ . The same type of pattern on the copolymerization diagram has been found in the copolymerization of VAc with N-acetoxyethylene maleimide [41], N-(2-propionyl oxyethyl)maleimide [42], N-(3-acetoxypropyl) maleimide [42], N-(n-butyl) maleimide [43], N-(chloroethyl) maleimide [43], and other N-maleimides [26, 43].

The third case is the copolymerization of NPMI-MMA, where the two monomer reactivity ratios are different,  $1 > r_1 = 0.183$  and  $1 < r_2 = 1.022$ ; one of the monomers is more reactive than the other toward both propagating species. The copolymer is richer in the more reactive monomer in random placement. In this case, the copolymer will have a tendency to contain more MMA than NPMI, since NPMI adds MMA more easily and MMA monomer has approximately the same tendency to react with both propagating species.

The  $r_1$  and  $r_2$  values for the three series of copolymers are summarized in Table 4 together with the existing values in the literature. The  $Q_1$  and  $e_1$  values of NPMI were calculated by using the Alfrey-Price equation with the values of  $r_1$  and  $r_2$  and by assuming the values for St, VAc, and MMA given by other authors [44]. The  $Q_1$  and  $e_1$  obtained for NPMI in the case of MMA agree fairly well with those obtained by Yamada et al. [45]. In order to draw conclusions on  $Q_1$  and  $e_1$ , the  $Q_1 - e_1$  values obtained on copolymerization of NPMI/St were not taken into account.

The  $Q_1$  and  $e_1$  values for this system tend to be large because of resonance effects of phenyl groups. Our values for  $Q_1$  and  $e_1$  were similar to those for other *N*-substituted maleimides [24, 42, 43].

The experimental results on the initial thermal stability temperature ( $T_i$ ) tabulated in Tables 1, 2, and 3 are plotted in Figs. 4 and 5, respectively. These results indicate that the thermal stability tends to increase as the NPMI content increases. In the series of NPMI-St copolymers the most profound effect of the nearly alternating copolymerization was found to be on the very moderate improvement of the relative thermal stability. Figure 4 shows the influence of the composition on the thermal stability. As can be seen, the copolymers have an almost alternating structure.

The behavior reflected in the relative thermal stability results suggests a higher stability because of the introduction of NPMI units into the main chain. Despite this, the stability is much more directly affected by the structural characteristics, perhaps because of the presence of 1,2-ethylenic units directly linked to the styrene units according to the degree of alternation. This feature leads also to the conclusion that this series of copolymers has a highly alternating nature, as we will subsequently see on considering glass transition temperatures.

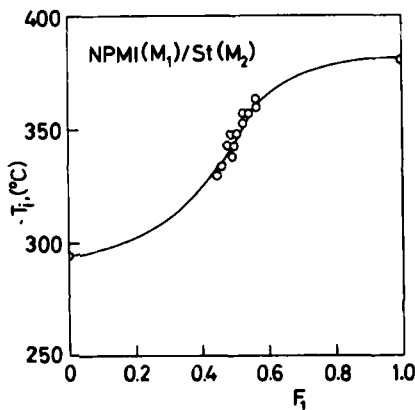


FIG. 4. Plot of initial relative thermal stability  $T_i$  against copolymer composition ( $F_1$ ) of a series of copolymers of *N*-phenyl maleimide ( $M_1$ )-styrene ( $M_2$ ) prepared by free-radical copolymerization in benzene at 35°C with AIBN as initiator.

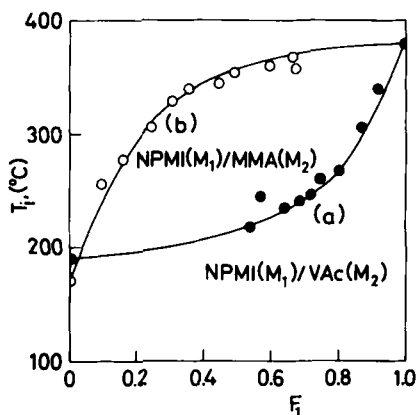


FIG. 5. Plots of initial relative thermal stability  $T_i$  against copolymer composition ( $F_1$ ) of a series of copolymers of (a) N-phenyl maleimide ( $M_1$ )-vinyl acetate ( $M_2$ ) and (b) N-phenyl maleimide ( $M_1$ )-methyl methacrylate ( $M_2$ ), both prepared by free-radical copolymerization in benzene at  $35^\circ\text{C}$  with AIBN as initiator.

Figure 6 shows plots of glass transition temperatures of NPMI-St copolymers against the monomer feed  $f_1$ . Little difference in the glass transition temperature was found in this composition range. These results also suggest that copolymers of NPMI-St possess more or less the same degree of alternation. This fact also indicates that the glass transition temperature is influenced very slightly by the composition and confirms that copolymerization is indeed nearly alternating.

The NPMI-MMA copolymers covered the complete composition range in weight fraction increments from 0.15 to 0.66, as can be seen on Table 3 and Fig. 7. This seemed a good series to examine with regard to the effect of the composition on the glass transition temperature.

Now the relationship between the glass transition temperature of random copolymers and the glass transition temperatures of the component homopolymers can be considered. The equation of Gordon and Taylor [46] is based on free volume concepts and it is expressed as follows:

$$(T_g - T_{g2})w_2 + k(T_g - T_{g1})w_1 = 0 \quad (1)$$



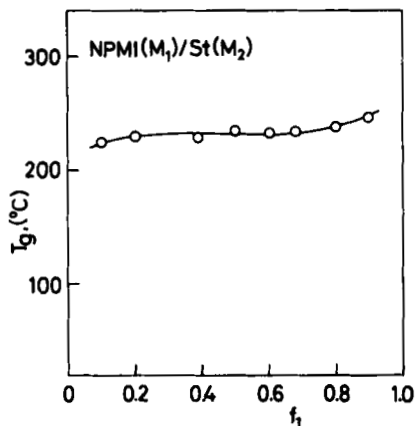


FIG. 6. Plot of glass transition temperatures (8° C/min by DSC) against monomer feed ( $f_1$ ) of a series of copolymers of N-phenyl maleimide ( $M_1$ ) with styrene ( $M_2$ ) prepared by free-radical copolymerization in benzene at 35° C with AIBN as initiator.

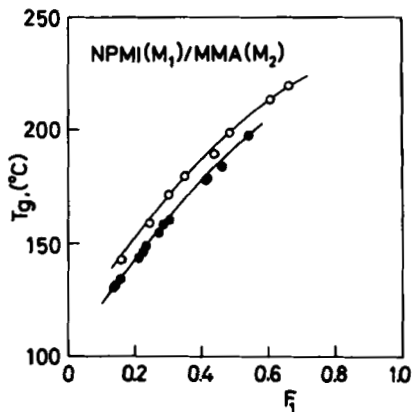


FIG. 7. Plots of (○) glass transition temperatures (8° C/min by DSC) against copolymer composition ( $F_1$ ) of a series of copolymers of N-phenyl maleimide ( $M_1$ ) with methyl methacrylate ( $M_2$ ), prepared by free-radical copolymerization in benzene at 35° C with AIBN as initiator; (●) glass transition temperatures (by dilatometry) from data of Aida et al. [2].

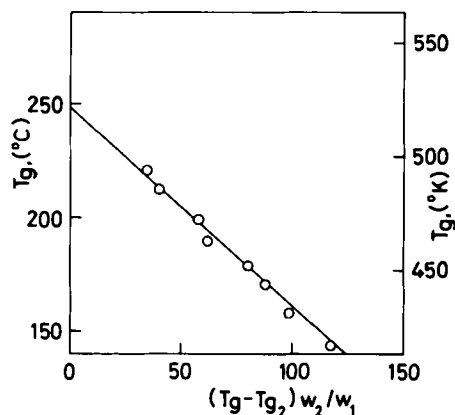


FIG. 8. Relation of glass transition temperature to composition according to a plot suggested by Eq. (1) for a series of copolymers of N-phenyl maleimide ( $M_1$ )-methyl methacrylate ( $M_2$ ) prepared by free-radical copolymerization in benzene at  $35^\circ\text{C}$  with AIBN as initiator.

where  $k$  is a function of the thermal expansion coefficients,  $w_1$  and  $w_2$  are weight fractions of homopolymers 1 and 2, and  $T_{g1}$ ,  $T_{g2}$ , and  $T_g$  are the glass transition temperatures of homopolymers 1 and 2 and their copolymers. Moreover, Eq. (1) should give the value for the  $T_g$  of pure poly(N-phenyl maleimide) ( $M_1$ ) when the weight fraction of the poly(methyl methacrylate) ( $M_2$ ) falls to zero. Then, if Eq. (1) holds for a copolymer, a plot of  $T_g$  against  $(T_g - T_{g2})w_2/w_1$  will be a straight line having a slope of  $-1/k$  and an intercept of  $T_{g1}$ . If such a plot is made with the experimental data for the NPMI/MMA random copolymer system in Fig. 8, a value of  $k = 1.16$  and  $T_{g1}$  for poly(N-phenyl maleimide) of  $248^\circ\text{C}$  are obtained if we assumed a value of  $105^\circ\text{C}$  for the glass transition temperature of heterotactic poly(methyl methacrylate) [47-50].

The apparent discrepancies found between the glass transition temperatures in this work and those of Aida et al. [2] are easily explained by keeping in mind the fact that our own values represent apparent glass transition values obtained at a rate of heating of  $8^\circ\text{C}/\text{min}$ , and those reported by Aida et al. [2] were obtained by dilatometry.

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