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Phenylacetylene-Methyl Acrylate Radical Copolymers

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ABSTRACT

Phenylacetylene (PA, M_2) and methyl acrylate (M_1) copolymerization can be described by the simple terminal model having the parameters $r_1 = 0.67$ and $r_2 = 0.11$. $^1\text{H-NMR}$ spectroscopy shows the predominant trans configuration of PA units, the high tendency of coisotactic alternating addition, and influence of temperature on the chain conformation.

INTRODUCTION

Radical copolymerization of phenylacetylene (PA, M_2) with methyl acrylate (MA, M_1) was studied by Doak [1], and the recalculated data according to the Kelen-Tüdös equation [2] confirmed the validity of the terminal copolymerization model [3]. The aim of this paper is to obtain configurational data for these copolymers.

EXPERIMENTAL

Copolymerizations were performed in bulk at 60°C under argon and with AIBN (1% from monomers) as initiator. The copolymers were separated by dissolution of the reaction mixture in benzene and precipitation with petroleum ether. Copolymer composition and configuration were determined from the $^1\text{H-NMR}$ spectra registered

TABLE 1. Copolymerization Data

Sample	$x = [M_1]/[M_2]$	Time (h)	Conversion (%)	$y = d[M_1]/d[M_2]$
1A	0.126	41.7	1.99	0.65
2A	0.252	41.6	3.59	0.79
3A	0.436	41.5	4.74	1.02
4A	0.678	41.4	6.31	1.28
5A	1.010	41.4	12.68	1.52
6A	1.494	29.0	9.83	1.97
7A	2.306	22.5	14.90	2.47
8A	3.392	22.5	19.00	3.18
9A	8.600	6.0	9.15	6.30

in $CDCl_3$ solutions at different temperatures on a JEOL C-60HL spectrometer operating at 60 MHz. The UV spectra ($CHCl_3$ solutions) were recorded on a Unicam SP 800 spectrophotometer. Copolymerization data are given in Table 1.

RESULTS AND DISCUSSIONS

Reactivity Ratio Determination

The copolymerization diagram for this system (Fig. 1) is of the type $r_1, r_2 < 1$. The Kelen-Tüdös plot ($\alpha = 0.54$) (Fig. 2) gives the results $r_1 = 0.67$ and $r_2 = 0.11$, very close to those given in the literature [1, 3] for the same polymerization conditions. However, the number of experiments was insufficient.

For this system as for MMA-PA [4], the straight line in the Kelen-Tüdös plot indicates the validity of the terminal copolymerization model. An attempt to use the Zaitsev equation [5] (Fig. 3) can possibly give the same values obtained by the Kelen-Tüdös method, but with a great subjective error.

The reactivity ratio values are used for diad and triad sequence fractions calculation according to Harwood's algorithm [6].

Copolymer Configuration

Methyl Acrylate Resonance

Figure 4 gives the saturated region of the 1H -NMR spectra with the resonance of MA structural units. The shielding influence of the PA

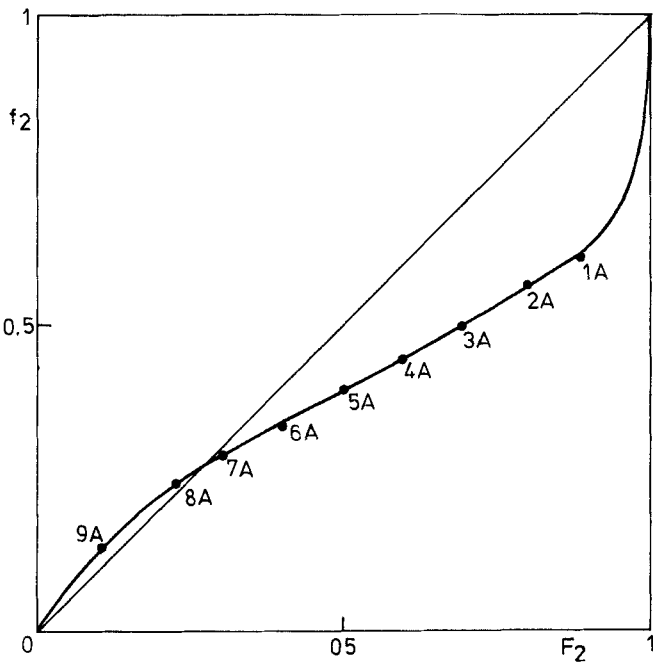


FIG. 1. Copolymerization diagram (F = molar fraction of the monomer in the initial mixture; f = structural unit fraction in copolymer).

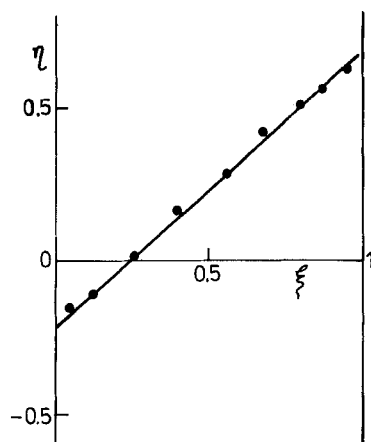


FIG. 2. The Kelen-Tüdös plot.

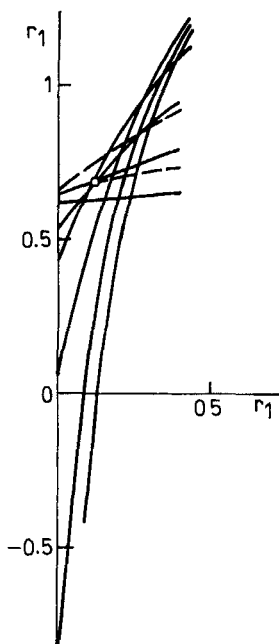


FIG. 3. The Zaitsev equation (the point corresponds to the values obtained by Kelen-Tüdös method).

structural units enchainment can be seen by the appearance and growing of some signals at higher fields when the PA content in the copolymer is increasing. They are assignable to the CH_2 protons from different tetrads in different configurations. Because the spectra are not completely resolved and the copolymer configuration is very complex, the quantitative analysis of the signals in this region could not be made.

The methoxy signal is split into three parts: A, B, and C. This splitting is lower than in the case of MMA-PA copolymers (this fact being analogous with the MA copolymers with styrene [7], 2-vinylpyridine [8], and 4-vinylpyridine [9]), and can be seen in the 4A-9A samples. The high-field shift of this signal as compared with poly(MA) is explained by the aromatic shielding effects of the neighboring PA units. The A, B, and C parts are obtained by elemental curve decomposition [10]. Using the same reasoning as in the case of MMA-PA copolymers [4], the applicability of the Ito [7]:

$$1/(1 - F_A^{\frac{1}{2}}) = (1/\sigma) + (r_1/\sigma)x \quad (1)$$

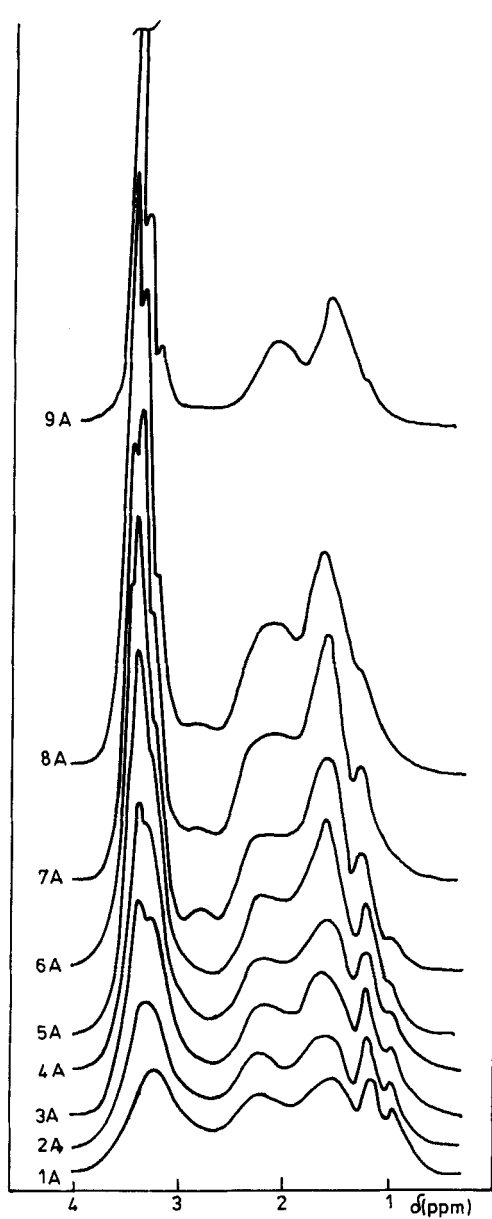


FIG. 4. Saturated region of $^1\text{H-NMR}$ spectra registered at 60°C .

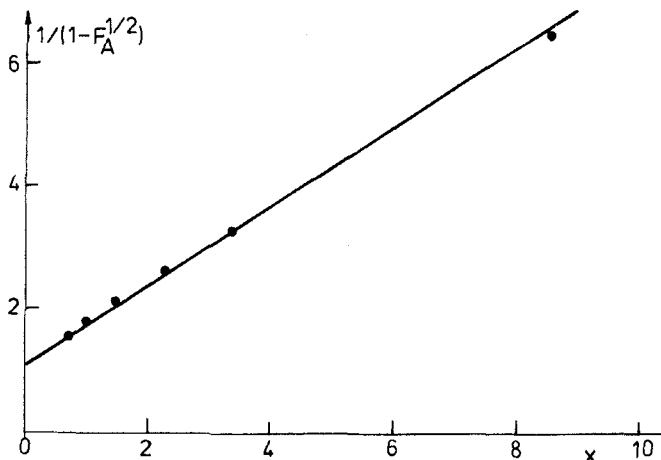


FIG. 5. Equation (1) plot.

and San Roman [11]:

$$(1 - F_A^{\frac{1}{2}}) = \sigma P_{12} \quad (2)$$

equations can be demonstrated. Here σ is the probability of obtaining a meso configuration in an alternating diad, F_A is the fraction of the A part from the methoxy signal, and P_{12} is the probability of PA adding to a MA-ended macroradical.

Figure 5 represents Eq. (1) and Fig. 6 Eq. (2); they give the value $\sigma = 0.9$ (and $r_1 = 0.6$). The probability of the existence of diads having the aromatic nucleus and the methoxy group on the same side of the main chain is, therefore, rather high, but, as for MMA-PA copolymers, it cannot be directly compared with the values obtained for other MA copolymers due to the configurational complexity introduced by the double bond of the PA structural units.

Phenylacetylene Resonance

The aromatic-olefinic region of the $^1\text{H-NMR}$ spectra, given in Fig. 7, presents the aromatic protons resonance at 7.08 ppm, a signal at about 5.2 ppm, and a continuous resonance, less intense, between these signals for the samples having a high PA content. The position of the highest field signal linearly depends on copolymer composition, as can be seen in Fig. 8. It is assigned, as in the case of MMA-PA copolymers [4], to the olefinic protons of 121 triads in trans to the aromatic nucleus. When comparing the fraction of 5.2 ppm signal

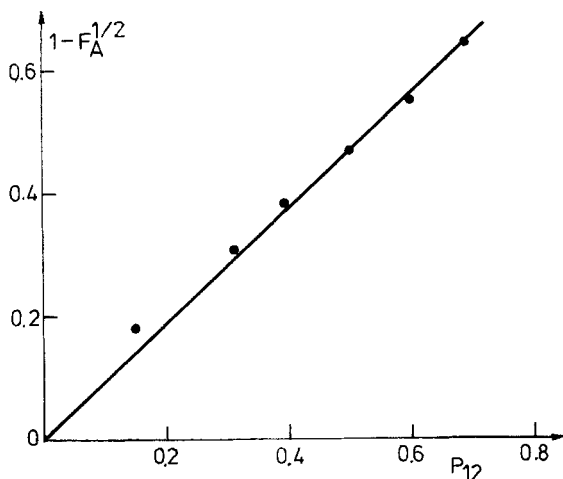


FIG. 6. Equation (2) plot.

with the calculated 121 triad fraction (Fig. 9), one can conclude that trans configuration also predominates for these copolymers. This fact is explained by the thermal isomerization tendency of the PA-ended macroradical from cis, as the triple bond is opened [12], to trans.

For these samples, 1,3- or 1,4-cyclohexadiene sequences cannot be excluded. They can appear at long reaction times and 60°C, as demonstrated for poly(PA) [12]. In the UV spectra, absorption is qualitatively shown between 320 and 340 nm [13] only for Sample 1A. However, the cyclohexadiene sequences must be of very low concentration because the calculated 222 fractions represent 21% from PA-centered triad fractions for Sample 1A, 9% for 2A, and below 5% for the others. The error introduced when the calculation is made without considering the cyclohexadiene units can be neglected because, of the 18 cyclohexadiene protons, only one (methynic) resonates in the saturated region.

Conformational Isomers

¹H-NMR spectra of Sample 5A, registered at four temperatures, are given in Fig. 10. Here also, besides the line broadening given by the viscosity, a high-field shift of the B and C parts from the methoxy signal is observed. Because the spectral resolution is rather poor, this shift is only qualitatively shown and cannot be measured. It is assigned to the conformational change from a more "stretched" form, deshielded, to a more "coiled" one, energetically

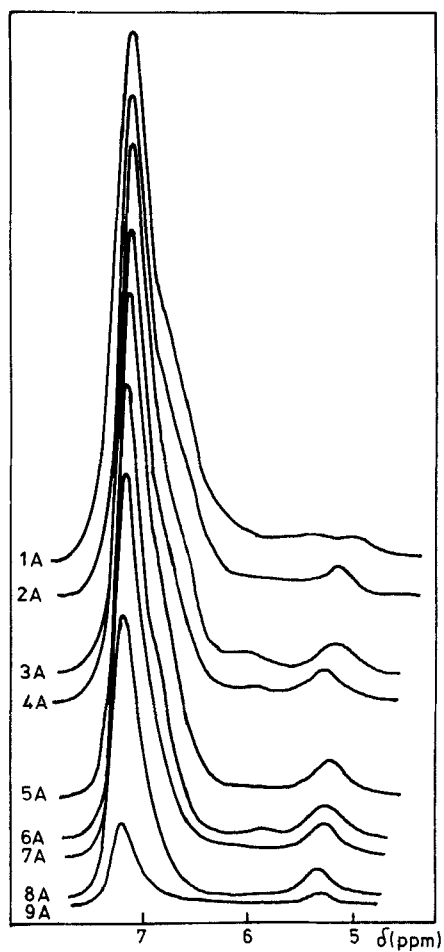


FIG. 7. Aromatic-olefinic region of $^1\text{H-NMR}$ spectra.

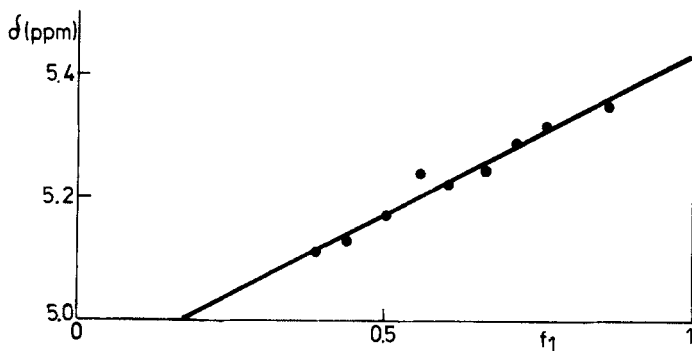


FIG. 8. Chemical shift of 121 trans triad CH= protons against copolymer composition.

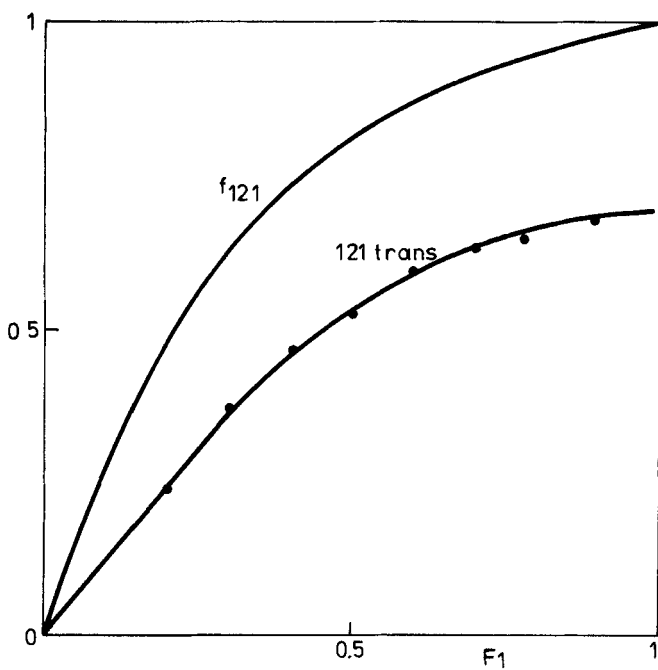


FIG. 9. Calculated 121 triad fraction and 121 trans sequences determined by NMR.

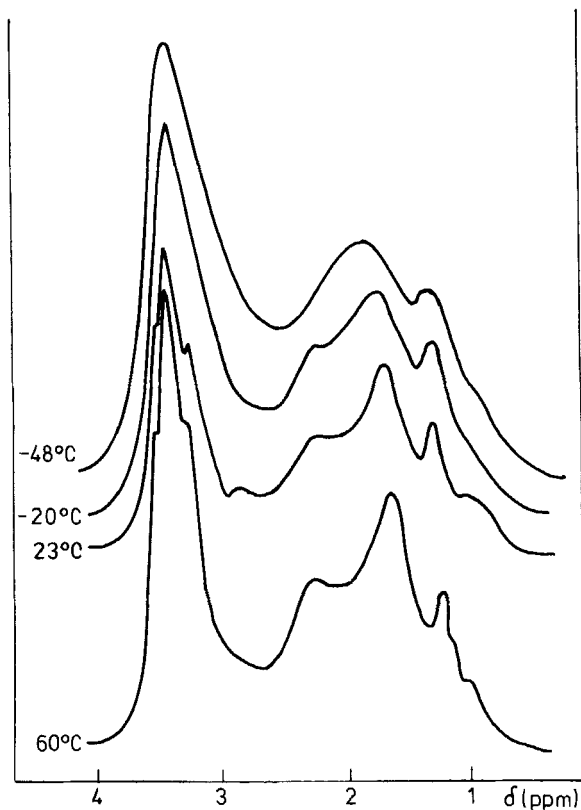


FIG. 10. ¹H-NMR spectrum of Sample 5A registered at four temperatures.

more stable, when the PA aromatic nuclei give maximum screening to the MA methoxy group [4].

CONCLUSIONS

Radical MA and PA copolymerization can be described by the simple terminal model. The PA-ended macroradical tendency to add MA is about ten times greater than the homopropagation tendency. The equation proposed by Zaitsev does not give more accurate or reliable reactivity ratio values.

The PA structural units are mainly in trans configuration, and this generates a chain with a geometry similar to a saturated one, unlike cis configuration. Therefore, the methoxy signal structure

is analogous to that obtained for other MA copolymers, and from the low-field fraction a marked preference for coisotactic addition can be determined, as for all MA copolymers given in the literature. The $^1\text{H-NMR}$ spectra evidence for conformational changes also changes with the temperature.

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