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Phenylacetylene-Methyl Methacrylate Radical Copolymers

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ABSTRACT

Radical copolymers of phenylacetylene (PA, M_2) with methyl methacrylate (M_1) can be characterized by the terminal copolymerization model with the parameters $r_1 = 1.07$ and $r_2 = 0.09$. By ^{1}H-NMR spectroscopy, the predominance of trans-configuration for PA structural units and a high tendency of coisotactic placement between the aromatic and methoxy groups are evidenced. Spectral changes with the registration temperature indicate conformational isomerism.

INTRODUCTION

Radical copolymerization of phenylacetylene (PA, M_2) with methyl methacrylate (MMA, M_1) was studied by Uzbekova et al. [1] and the reactivity ratios determined. The recalculated reactivity ratios by the Kelen-Tüdös method [2] had no physical significance [3]. The aim of this paper is to study this copolymerization system and also to obtain configurational and conformational data.

EXPERIMENTAL

Copolymerizations were performed in bulk at 60°C under argon and with AIBN (1% from monomers) as initiator. The conversion was

TABLE 1. Copolymerization Data

Sample	$x = [M_1]/[M_2]$	Time (h)	Conversion (%)	$y = d[M_1]/d[M_2]$
1M	0.126	114.0	2.09	0.63
2M	0.263	52.7	1.43	0.99
3M	0.468	21.0	1.50	1.30
4M	0.669	22.0	4.19	1.61
5M	1.024	4.0	1.22	2.15
6M	1.500	7.5	4.76	2.78
7M	2.300	2.0	1.36	3.40
8M	3.926	1.5	1.53	4.98
9M	8.174	1.1	2.25	9.45

kept under 5%. The copolymers were separated by dissolution of the reaction mixture in benzene and precipitation with methanol having a small amount of HCl. Copolymer composition and configuration were determined from the ^1H-NMR spectra of $CDCl_3$ solutions at different temperatures on a JEOL C-60HL spectrometer operating at 60 MHz. The UV spectra were registered in $CHCl_3$ solutions 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 belongs to the case $r_1 > 1$, $r_2 < 1$ (Fig. 1). In order to verify the validity of the terminal copolymerization model and to determine the reactivity ratio values, the Kelen-Tüdös equation [2] is used ($\alpha = 0.42$). From the straight line obtained (Fig. 2), the values are $r_1 = 1.07$ and $r_2 = 0.09$. The straight line indicates the validity of the terminal copolymerization system, and the values obtained are used for addition probabilities and triad fractions calculation according to Harwood's algorithm [4].

The copolymerization equation proposed by Zaitsev [5] for vinylic and acetylenic monomers gives the plot in Fig. 3. As it is clear in the figure, the lines intersect in a region, one of its points being the result of the Kelen-Tüdös equation. Therefore, one cannot conclude that the Zaitsev equation gives more precise or reliable values for reactivity ratios.

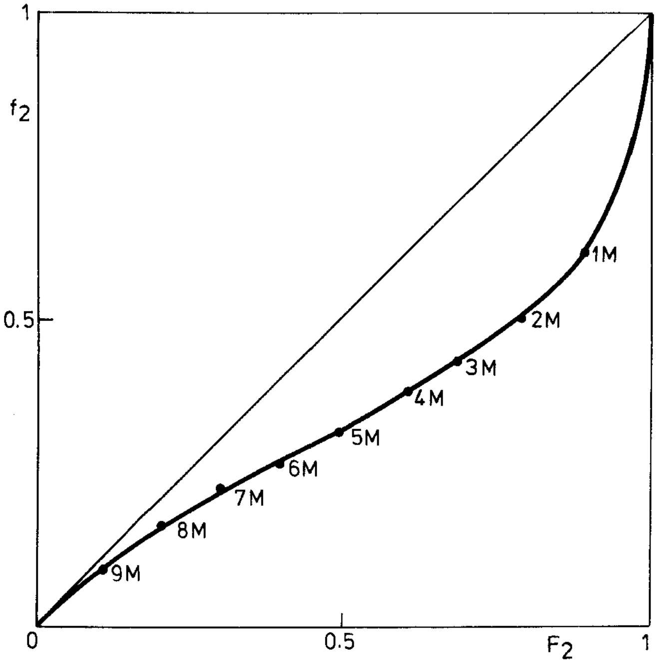

FIG. 1. Copolymerization diagram (F = monomer fraction in the initial mixture; f = structural unit fraction in copolymer).

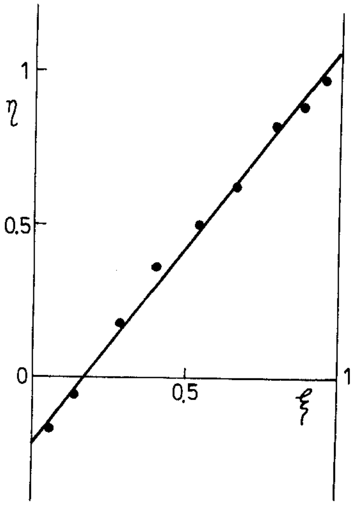

FIG. 2. The Kelen-Tüdös plot.

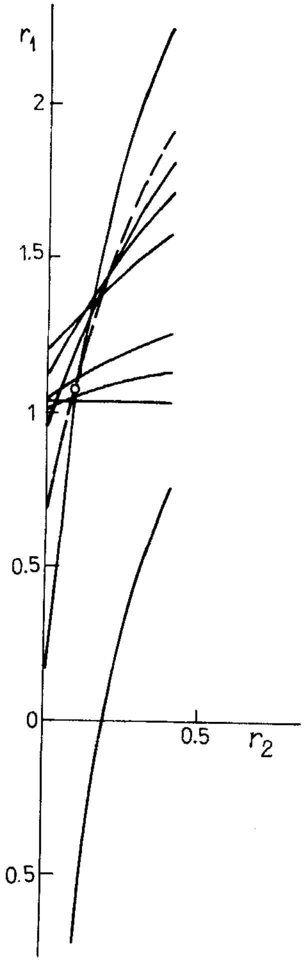

FIG. 3. The Zaitsev equation (the point corresponds to the values obtained by the Kelen-Tüdös method).

Copolymer Configuration

Methyl Methacrylate Resonance

Figure 4 gives the saturated region of the ^{1}H-NMR spectra registered at 60°C. This region represents the MMA structural unit's resonance. One can identify αCH_3, CH_2, and OCH_3 resonances; the last two overlap. The methoxy signal can be divided into three parts:

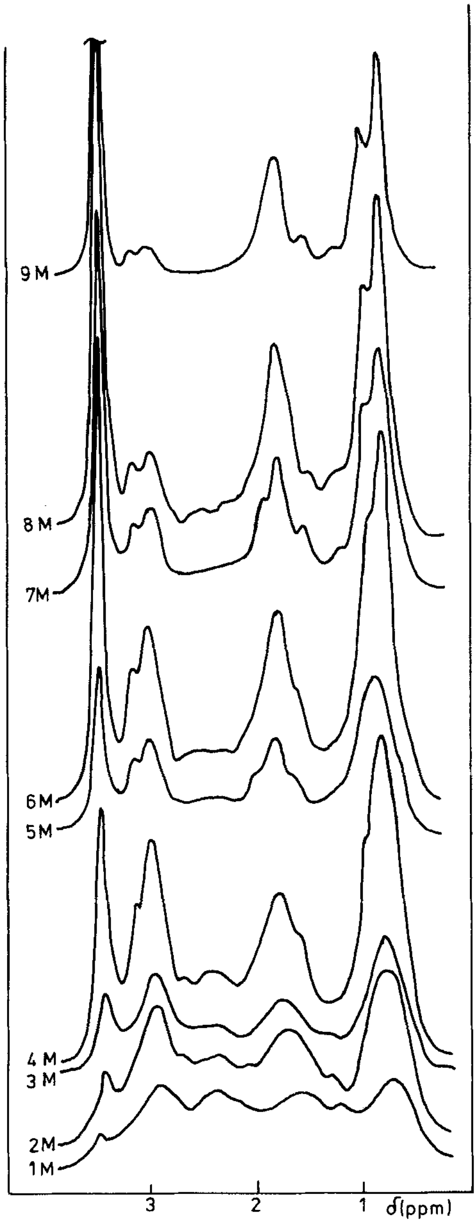

FIG. 4. Saturated region of ^{1}H-NMR spectra registered at 60° C.

A, B, and C with increasing field. Their assignment can be made by analogy with the methoxy resonance of other MMA copolymers [6], considering that the high-field shift as compared with methoxy resonance in poly(MMA) is determined by the near-neighboring aromatic nuclei screening effect. Generally, more remote units effects are neglected, together with the substitution effect for the three possible types of MMA-centered triads.

The PA copolymers have yet another asymmetry center on the main chain–the double bond–and this changes the chain geometry. Therefore, one cannot make the usual assignments for A, B, and C. However, the A part can be considered to be due to the MMA-centered triads with no screening effect, i.e., 111, 2_r11, and 2_r1_r2 (r indicates racemic configuration, the aromatic nucleus and the methoxy group being opposed, and m indicates meso configuration).

Then the Ito [6]:

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

and San Roman [7]:

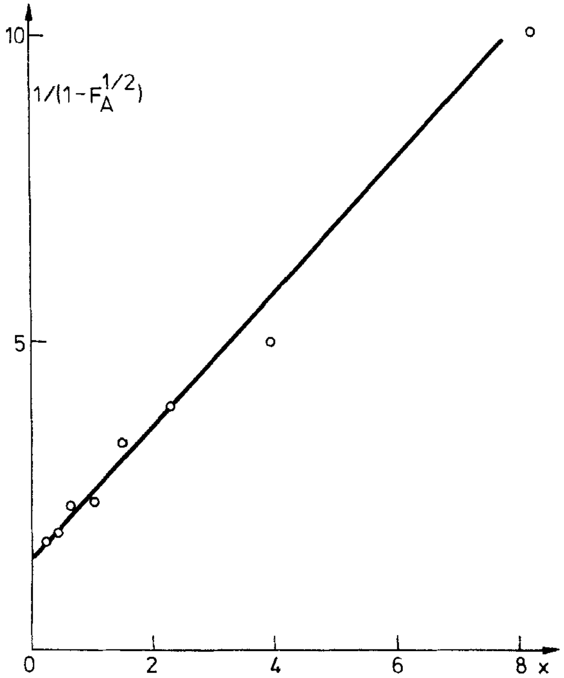

FIG. 5. Equation (1) plot.

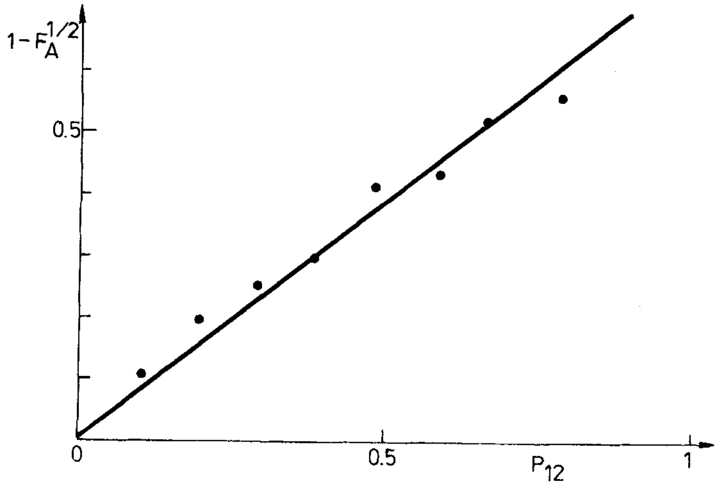

FIG. 6. Equation (2) plot.

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

equations can be applied. Here σ is the probability of obtaining a meso configuration in an alternating diad and P_{12} is the probability of PA addition at a MMA-ended macroradical.

The plots of Eqs. (1) (Fig. 5) and (2) (Fig. 6) give the value $\sigma = 0.8$ (and $r_1 = 0.95$, rather close to the real one).

For all signals in this region, a high-field shift is observed when there is increasing PA content in the copolymer (Fig. 7). A similar shift was observed for styrene-MMA copolymers [7] and assigned to the increased shielding effects of the aromatic nuclei.

Phenylacetylene Resonance

Figure 8 represents the aromatic-olefinic region of the ^{1}H-NMR spectra. The aromatic protons resonate at 7.08 ppm. There is also a signal at about 5.2 ppm. The chemical shift of this signal linearly depends on copolymer composition (Fig. 9). Its assignment is made by chemical shift calculation [8] and by analogy with micromolecular compounds: It is the CH= protons resonance from PA structural units of 121 triads and in trans configuration to the aromatic nucleus. The chemical shift calculation for the other triads in cis or trans configurations gives values between 6.9 and 5.8 ppm (the most shielded being the 121 cis triad at 5.8 ppm). In the spectra of samples having high PA content, there is an almost continuous signal between 7 and 5 ppm, and this indicates the resonance of CH= protons in different triads and configurations.

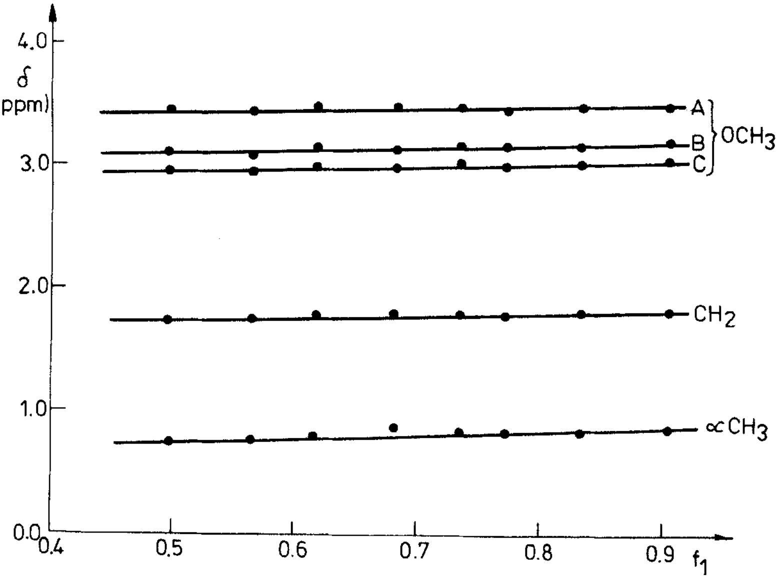

FIG. 7. Chemical shift of saturated region signals against copolymer composition.

As it is already known [9, 10], radical or coordinative polymerization of PA takes place by cis opening of the triple bond. The heat of polymerization and the temperature of polymerization determine, especially during the propagation reaction, the cis-trans isomerization and the intramolecular cyclization giving 1,3-cyclohexadiene units or 1,4-cyclohexadiene chain ends. When the concentration of cyclohexadiene sequences is too low to be determined by NMR (and this is our case), they can be evidenced by their UV characteristic absorption between 320-340 nm [11]. For all MMA-PA copolymer samples, this absorption is not present, unlike in methyl acrylate-PA copolymers [12].

Figure 10 represents the calculated 121 triad fraction and the 121 trans sequences concentration determined from the 5.2 ppm signal. As expected, trans configuration is preferred to cis, mainly due to the reaction conditions, for the temperature determines cis-trans isomerization during propagation.

The steric models of 12 diads for the two possible PA configurations (Fig. 11) prove the much higher shielding effect in the 1_m2 trans diad as compared with the 1_m2 cis, and this explains why the three parts of the methoxy signal (A, B, and C) do not have their usual shape and splitting (0.5 ppm). The B and C parts are composed of different

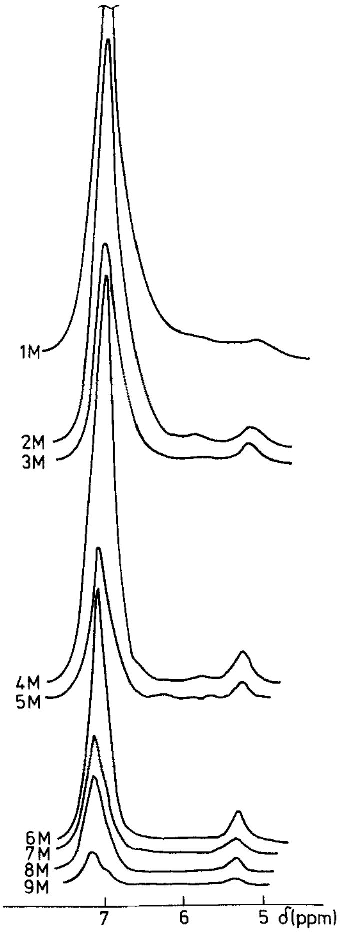

FIG. 8. Aromatic-olefinic region of ^{1}H-NMR spectra.

triads mixtures in cis and trans configurations, with more trans, but having chemical shifts closer to each other compared with vinylic monomers.

Conformational Isomers

The saturated region of the ^{1}H-NMR spectra (Sample 5M) registered in $CDCl_3$ at four temperatures is presented in Fig. 12. Together with the broadening of all signals given by the increased viscosity at small temperatures, one can observe the shift of the C part from the methoxy

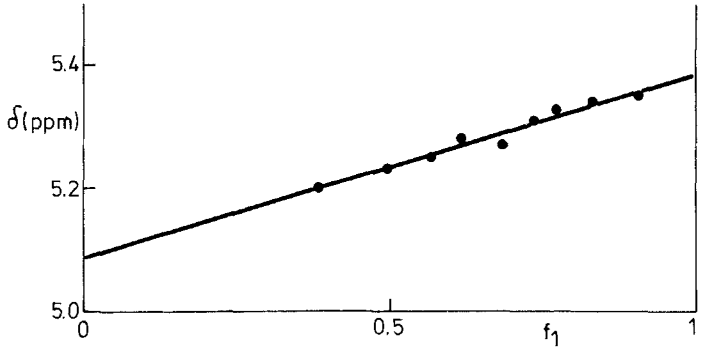

FIG. 9. Chemical shift of 121 trans triad CH= protons against copolymer composition.

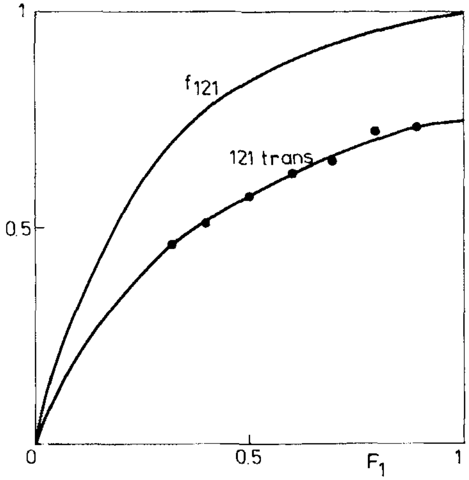

FIG. 10. Calculated 121 triad fraction and 121 trans sequences determined by NMR.

signal to a higher field. This shift is determined by the increase of the aromatic shielding effect. Because the C part is generally assigned to a double-shielded methoxy group [6], the steric model of the 2_m1_m2 trans triad is represented in two conformations: the most stretched one and the conformation having the greatest shielding effect (Figs. 13a and 13b). Therefore, the high-field shift with decreasing temperature can be explained by the reduced segmental

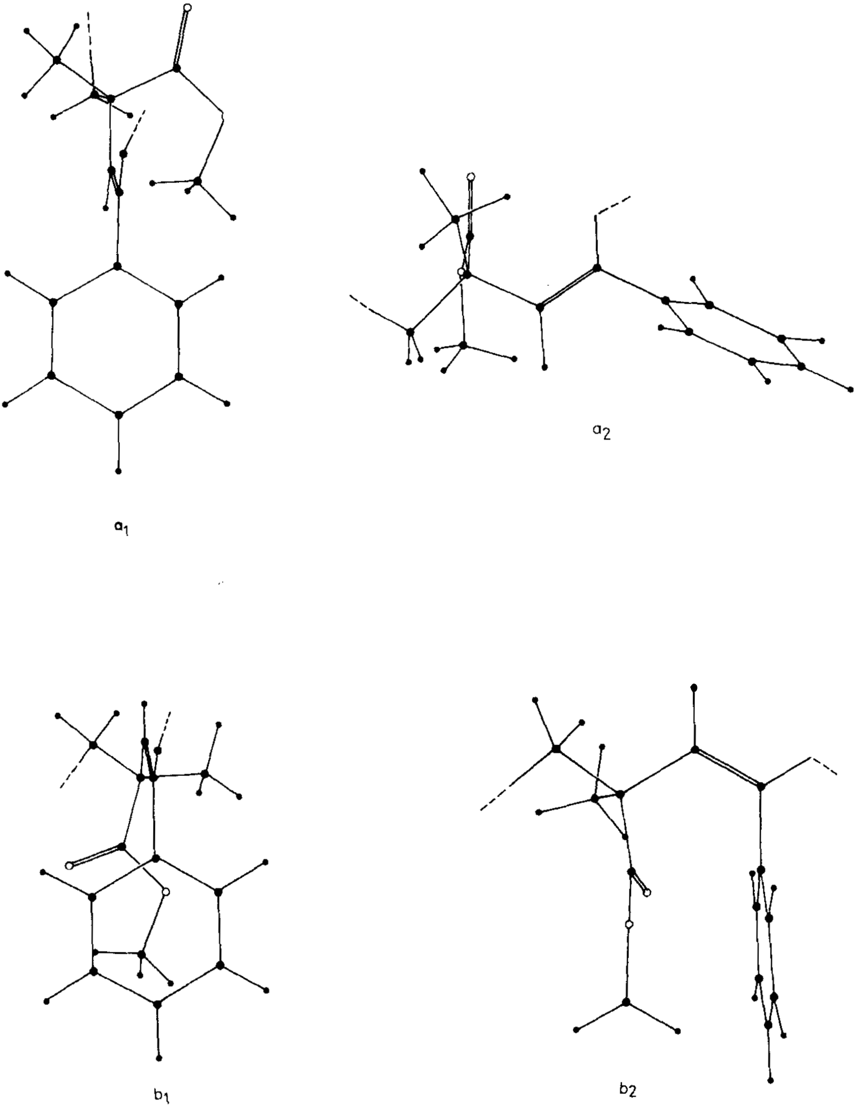

FIG. 11. Steric models for 1_m2 trans (b) and 1_m2 cis (a) diads.

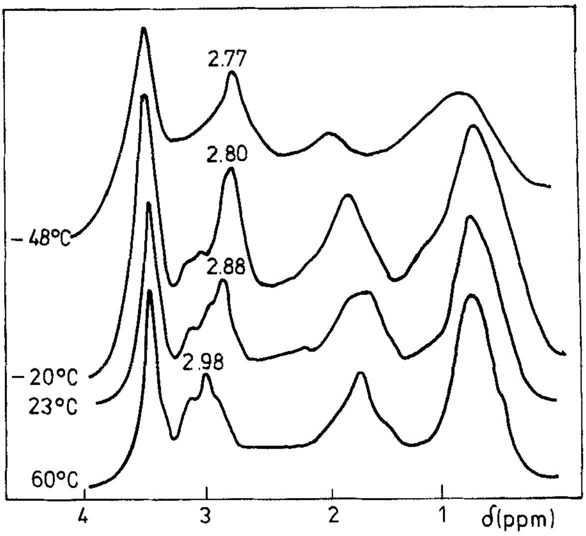

FIG. 12. ^{1}H-NMR spectrum of sample 5M registered at four temperatures.

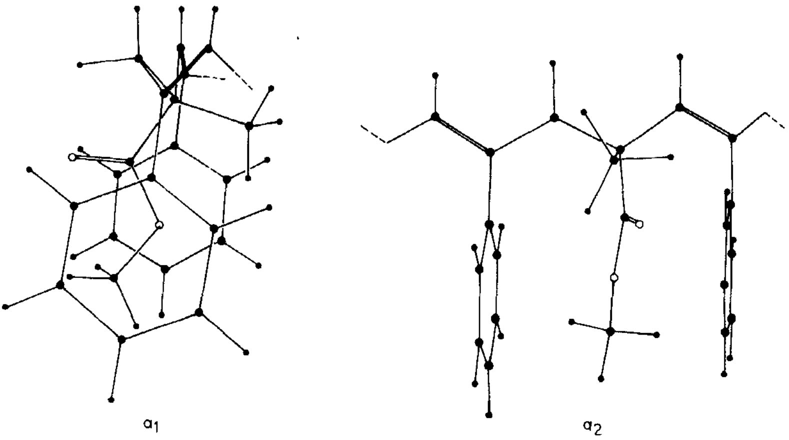

FIG. 13a. Steric models of 2_m1_m2 trans triad in the most shielded conformations.

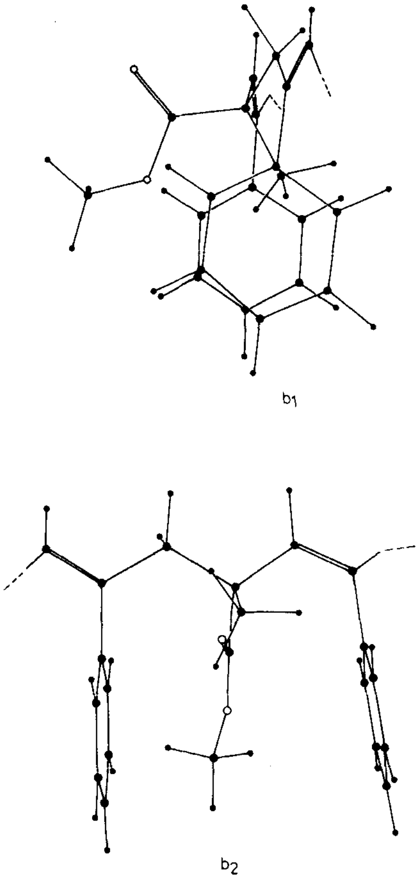

FIG. 13b. Steric models of 2_m1_m2 trans triad in the stretched conformations.

mobility with a preference for a more "coiled" form, less stretched, whose geometry permits a higher shielding effect.

CONCLUSIONS

Phenylacetylene and methyl methacrylate form a radical statistic copolymer. Copolymerization data verify the Kelen-Tüdös equation; therefore the copolymerization mechanism is correctly approximated by the simple terminal model. The Zaitsev equation does not give other reactivity ratio values; therefore the copolymerization is not inhibited when the PA-ended macroradical has longer PA sequences. However, the probability of obtaining such sequences is very low because PA has a ten times greater tendency to add MMA than to generate a 22 sequence. For samples with a high PA content in the initial mixture, diad and triad PA fractions grow, but, even for Sample 1M, $f_{222} = 0.174$.

Unfortunately, there is no possibility to determine the sequence fractions directly in the NMR spectra.

The configuration of the copolymers obtained is a complex problem because there are two asymmetry centers on the main chain: the double bond and the quaternary carbon. Phenylacetylene polymerizes by cis opening of the triple bond, but, even in adequate thermal conditions [9], the cis configuration percent in poly(PA) is rarely above 90%. Thermal radical copolymerization mainly generates trans PA structural units, and this means that cis-trans isomerization takes place easily even if the terminal PA has a MMA penultimate unit. The enchained PA in the 121 sequences does not isomerize, even in hard thermal conditions. This is proved by heating the copolymer samples in hexachlorobutadiene at 200° C; the ratio aromatic:5.2 ppm signals remain unchanged. This confirms the fact that cis-trans isomerization takes place mainly during the propagation reaction. Thermal isomerization cis-cyclohexadiene, as it occurs in poly(PA) [9], is extremely improbable due to the very low 222 triad fractions.

The σ-value obtained from the A fraction of the methoxy signal is a rather big one. It must be emphasized that this value cannot be directly compared with others obtained for vinylic copolymers because the chain configuration significantly differs due to the cis-trans isomery of the PA units. Moreover, the influence of more remote units cannot be excluded as was evidenced for MMA copolymers with p-chlorostyrene [13], 2-vinylpyridine [14], and 4-vinylpyridine [15].

By the registration of ^{1}H-NMR spectra at different temperatures, spectral differences due to conformational isomers are shown. These are explained by an increase of the aromatic shielding effect in the more "coiled" form of the chain, energetically preferred.

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