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The NMR Spectra of Styrene-Itaconate Ester Copolymers Obtained by Free Radical Mechanism

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SUMMARY

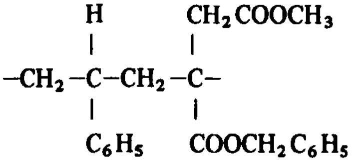
Styrene copolymerized with dimethyl itaconate and with methyl benzyl itaconate by use of a free radical initiator.

Monomer reactivity ratios for styrene (M_1)-dimethyl itaconate (M_2) copolymerization were $r_1 = 0.50$ and $r_2 = 0.06$ and for styrene (M_1)-methyl benzyl itaconate (M_2), $r_1 = 0.42$ and $r_2 = 0.19$. The nonconjugative methoxycarbonyl affected the monomer reactivity of itaconate toward polystyrene radical.

The NMR spectra of styrene-dimethyl itaconate copolymers were very complex and could not be interpreted because the two methoxy groups have similar chemical shifts.

The NMR spectra of styrene-itaconate copolymers were not so complex if methyl benzyl itaconate was used as comonomer instead of dimethyl itaconate. Methoxy and benzyloxy absorptions were sufficiently separated and "co-isotacticity" could be determined.

"co-isotacticity" $\sigma = 0.5$

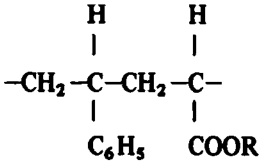


$$-CH_2-\underset{C_6H_5}{\overset{H}{C}}-CH_2-\underset{COOCH_2C_6H_5}{\overset{CH_2COOCH_3}{C}}-$$

It is shown that the nonconjugative methoxycarbonyl group had little influence on the steric course of the cross-propagation reaction between styrene and itaconate.

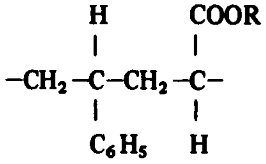
INTRODUCTION

The styrene-acrylic ester copolymers obtained by free radical mechanism have been well characterized with high-resolution nuclear magnetic resonance spectroscopy (NMR) by Ito et al. [1]. They described the copolymer microstructure using the monomer reactivity ratios (r_1 and r_2) and the "co-isotacticity" σ. The latter indicates the probability that the alternating styrene unit and acrylic ester unit take the same ("co-isotactic") configuration.



$$-CH_2-\overset{\displaystyle H}{\underset{\displaystyle C_6H_5}{C}}-CH_2-\overset{\displaystyle H}{\underset{\displaystyle COOR}{C}}-$$

probability σ

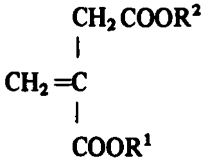


$$-CH_2-\overset{\displaystyle H}{\underset{\displaystyle C_6H_5}{C}}-CH_2-\overset{\displaystyle COOR}{\underset{\displaystyle H}{C}}-$$

probability $1 - \sigma$

For example, the styrene-methyl acrylate copolymer was described by $r_1 = 1.0$, $r_2 = 0.16$, and $\sigma = 0.80$ (styrene is M_1 comonomer and methyl acrylate is M_2 comonomer). The high σ was understood as an attractive interaction operated between the phenyl group and the methoxycarbonyl group.

In this paper, the microstructure of styrene-itaconate ester copolymers is discussed from the point of view of their NMR spectra. An itaconate ester (I) can be



$CH_2{=}C(COOR^1)CH_2COOR^2$

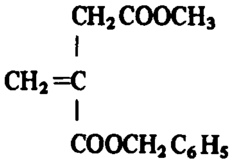
(I)

regarded as an α-alkoxycarbonylmethyl ($-CH_2COOR^2$)-substituted acrylic ester. It appeared of interest to investigate the role of this additional, nonconjugative alkoxycarbonyl group in the steric course of cross-propagation reaction in the copolymerization with styrene.

EXPERIMENTAL

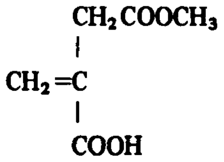
Dimethyl itaconate was prepared from itaconic anhydride by refluxing in methanol with a small amount of concentrated sulfuric acid, bp, 99-105°C/14 mmHg; mp, 34.8-36.2°C (lit. [2], 36.4-37.3°C).

Methyl benzyl itaconate (II) was prepared from itaconic acid as follows. Itaconic acid (124 g), methanol (123 ml), and acetyl chloride (2 ml) were refluxed for 15 min [3]. The reaction mixture was rapidly distilled under reduced pressure. The fraction boiling between 118 and 170°C/30-25 mmHg was collected and was crystallized on standing. Crude



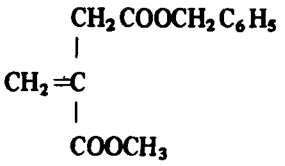
$CH_2{=}C(COOCH_2C_6H_5)CH_2COOCH_3$

(II)



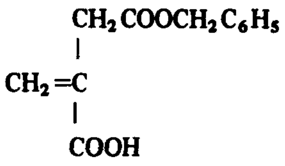
$CH_2{=}C(COOH)CH_2COOCH_3$

(III)



$CH_2{=}C(COOCH_3)CH_2COOCH_2C_6H_5$

(IV)



$CH_2{=}C(COOH)CH_2COOCH_2C_6H_5$

(V)

methyl hydrogen itaconate (III) was recrystallized from a benzene-ligroin mixture: yield, 90 g, 66%; mp, 66.5-69.0°C (lit. [3], 66-68°C); neutralization equivalent, found 143.4 (calcd. 144.1). Methyl hydrogen itaconate (III) (175 g) in methanol (200 ml) was neutralized to phenolphthalein with potassium hydroxide (68.5 g) in methanol (200 ml) at 5-10°C. The solvent was evaporated in vacuum. Methyl potassium itaconate solidified. Methyl potassium itaconate (108.4 g) was heated with benzyl chloride (350 ml) and trimethylbenzylammonium chloride (1.5 g) with stirring at 110-125°C for 2 hr. The excess benzyl chloride was distilled off and methyl benzyl itaconate (II) was distilled at 161-162°C/7 mmHg: yield, 79 g, 57%; $n_D^{20^\circ C}$, 1.5100; saponification equivalent, found 481.5 (calcd. 479.8); carbon %, found 66.66 (calcd. 66.84); hydrogen %, found 6.26 (calcd. 6.02). The gas chromatogram for this sample showed only one peak on Apiezon L, dioctyl phthalate, and polyethylene glycol columns at 200°C with 80 ml of H_2 carrier gas.

The isomeric benzyl methyl itaconate (IV) (the nomenclature of these two isomers used here is arbitrary) was also prepared for comparison. Itaconic acid (65 g), benzyl alcohol (162 g), and acetyl chloride (5 ml) were refluxed for 5 hr. The excess benzyl alcohol was distilled off at a reduced pressure and the residual benzyl hydrogen itaconate was recrystallized from acetone: yield, 55 g, 48%; mp, 86.5-88.0°C; neutralization equivalent, found 252.7 (calcd. 255.0); carbon %, found 65.63 (calcd. 65.45); hydrogen %, found 5.62 (calcd. 5.49). Benzyl hydrogen itaconate (V) (22 g) in ether (100 ml) was reacted with ethereal solution of equivalent diazomethane. Pure benzyl methyl itaconate (IV) was obtained after the distillation of the reaction mixture, bp, 126.0-126.5°C/1 mmHg; yield, 17 g, 73%. The gas chromatograms of this sample showed only one peak, and showed distinct, distinguishable retention times from that of the isomeric methyl benzyl itaconate on three columns. Infrared spectra of the two isomeric esters were also clearly different. Methyl benzyl itaconate gave $\nu_{C=O}$ absorptions at 1747 cm^{-1} (nonconjugative) and 1722 cm^{-1} (conjugative), and benzyl methyl itaconate gave a superimposed absorption at 1740 cm^{-1}.

Commercial styrene was successively washed with 10% sodium hydroxide and distilled water, dried over calcium chloride, and fractionated under nitrogen.

Copolymerization was conducted at 60°C. Five grams of a styrene-itaconate ester mixture and 20 mg of azobisisobutyronitrile were heated for a few hours and poured into 100 ml of methanol. The white, powdery copolymer was dissolved in benzene and again reprecipitated with methanol. The copolymer was freeze-dried from benzene solution and dried in a vacuum desiccator to a constant weight. The copolymer composition was calculated from the carbon assay and the NMR peak area ratio. Two methods of determination agreed well. The Fineman-Ross method was used to obtain the monomer reactivity ratios.

NMR spectra of the copolymers were run on JEOL C-60 and Hitachi R-20 spectrometers at 70°C in carbon tetrachloride (10 w/v%).

RESULTS AND DISCUSSION

Styrene-Dimethyl Itaconate Copolymer

Copolymerizations of styrene-dimethyl itaconate gave monomer reactivity ratios of $r_1 = 0.50$ and $r_2 = 0.06$, where suffix 1 refers to styrene and 2 to dimethyl itaconate (Fig. 1). This result agrees well with those reported for this system, $r_1 = 0.48$ and $r_2 = 0.14$ [4]. The reciprocal of r_1 represents a relative reactivity of dimethyl itaconate monomer toward styrene polymer radical ($1/r_1 = k_{12}/k_{11}$). Chikanishi and Tsuruta [5] reported a linear correlation between log $1/r_1$ and Taft's steric substituent constant E_S [6] of the α-alkyl substituent R of a series of α-alkyl acrylates in their copolymerization with styrene. When $R = CH_2C_6H_5$, the inductive effect

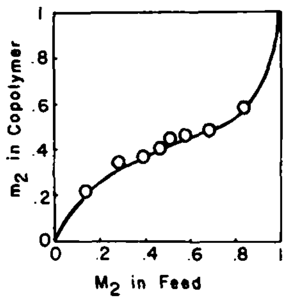
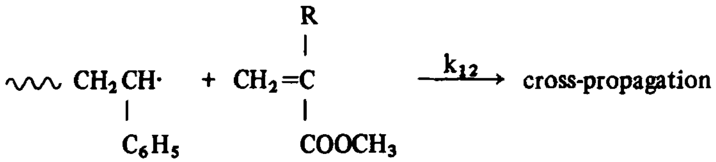


Fig. 1. Copolymerization of styrene (M_1) and dimethyl itaconate (M_2); abscissa: M_2 mole fraction in comonomer feed; ordinate: m_2 mole fraction in copolymer.



$$\sim\sim\; CH_2\underset{\displaystyle C_6H_5}{\underset{|}{CH\cdot}} \; + \; CH_2{=}\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle COOCH_3}{\underset{|}{C}}}} \xrightarrow{k_{12}} \text{cross-propagation}$$

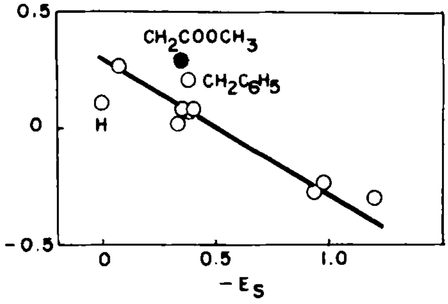


Fig. 2. Reactivity of methyl α-alkyl acrylate $CH_2=C(R)COOCH_3$ toward styrene polymer radical. E_S in abscissa denotes Taft's steric substituent constant for RCH_2-.

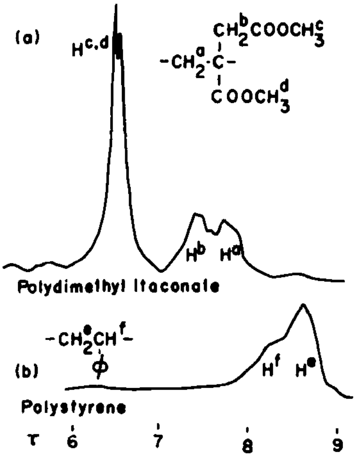


Fig. 3. NMR spectra of (a) polydimethyl itaconate and (b) polystyrene in carbon tetrachloride (10 w/v %) at 70°C.

of phenyl group influenced the cross-propagation reaction and thus the plot of methyl α-benzyl acrylate deviated from the correlation line. Dimethyl itaconate can be considered as a methyl α-alkyl acrylate where the α-alkyl substituent is a methoxycarbonylmethyl group ($-CH_2COOCH_3$). Taft's steric substituent constant for this group is unfortunately unknown. However, it should not differ greatly from the value for isobutyl group, -0.35 [6]. With this estimation, the experimental result for dimethyl itaconate was plotted on Tsuruta's correlation in Fig. 2 (symbol ●). It deviated

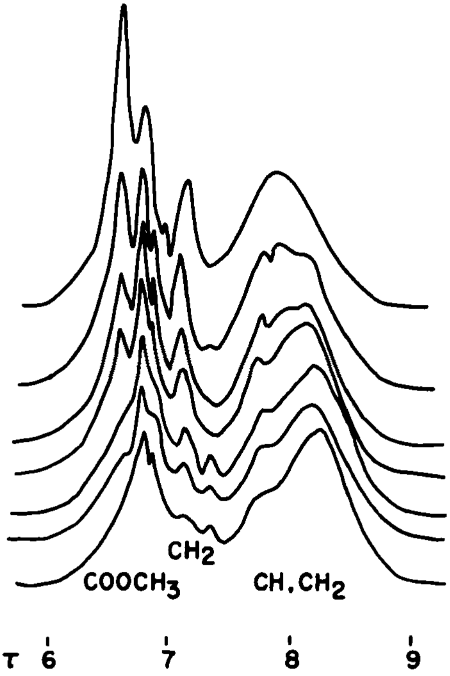


Fig. 4. NMR spectra of styrene-dimethyl itaconate copolymers in carbon tetrachloride (10 w/v %) at 70°C.

above the line, indicating that the inductive and steric effects of methoxycarbonylmethyl group both affected the rate of cross-propagation reaction. Similar deviations from the correlation line were reported by us [7] for methyl α-chloro- and α-bromoacrylates, and the role of halogen atom was discussed.

The NMR spectrum of polydimethyl itaconate was also recorded for comparison and is shown in Fig. 3(a). Two sharp singlets appear at 6.5 τ and two broad and low peaks between 7 and 8 τ. The chemical shift of 6.5 τ was assigned to the methyl protons of the two methoxycarbonyl groups. We assigned the lower field peak at 6.5 τ to the more easily rotatable methoxycarbonyl group attached to the side chain methylene group, and the low field broad peaks between 7 and 8 τ to the two kinds of methylene groups. The absorption at the lower magnetic field is of the side chain methylene group that is flanked by a methoxycarbonyl. The NMR spectrum of polystyrene is shown in Fig. 3(b) for comparison (phenyl protons at 3-4 τ are not shown).

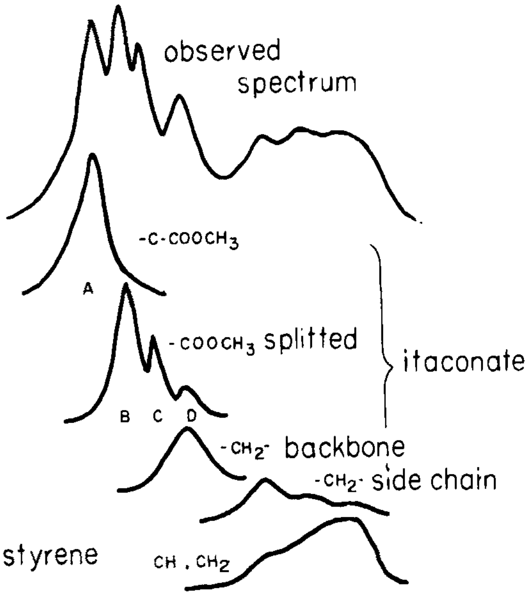


Fig. 5. Interpretation of observed spectra of styrene-dimethyl itaconate copolymer.

The NMR spectra of styrene-dimethyl itaconate copolymers in Fig. 4 are not simple superpositions of the spectra of polydimethyl itaconate [Fig. 3(a)] and polystyrene [Fig. 3(b)]. The spectra in Fig. 4 are arranged according to increasing styrene content. The phenyl protons at 3.1 τ, which increase their intensities with increasing styrene content, are again not shown. The two methoxycarbonyl protons of dimethyl itaconate unit show many peaks at 6-7 τ. The absorptions at 7-7.5 τ are assigned to the side chain methylene group of the dimethyl itaconate unit. The peaks due to the dimethyl itaconate unit decrease their individual peak areas and split into many peaks as the dimethyl itaconate unit decreases its content in the copolymer. The absorption at 7.5-9 τ was assigned to the methylene and methine groups of the styrene unit and the backbone methylene group of the dimethyl itaconate unit. The summit of the absorption shifts to the higher magnetic field as the styrene content increases.

Styrene-methyl methacrylate copolymers have been studied in detail by NMR [1]. The methyl and methoxycarbonyl protons shift to the higher magnetic field and the signal splits into several peaks as the neighboring "co-isotactic" styrene unit increases. Its cause was ascribed to

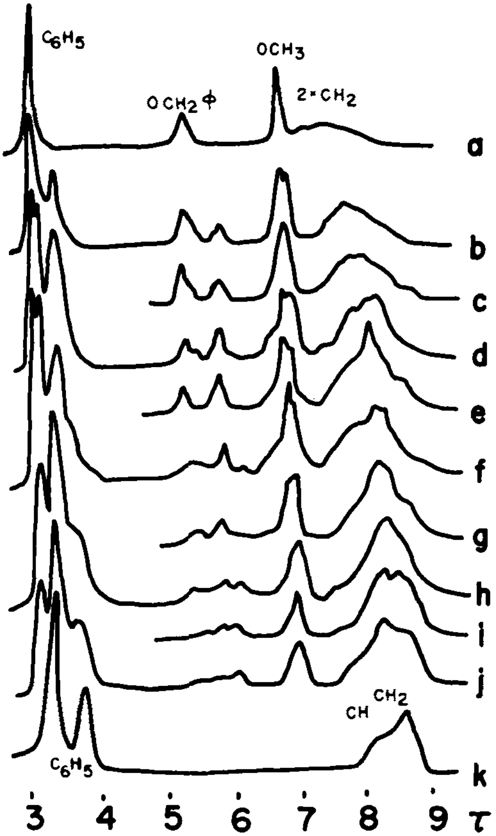


Fig. 6. NMR spectra of styrene-methyl benzyl itaconate copolymers in carbon tetrachloride (10 w/v %) at 70°C. (a) Polymethyl benzyl itaconate, (b-j) styrene-methyl benzyl itaconate copolymer, (k) polystyrene.

the anisotropic shielding by the benzene π-electrons in the styrene unit. We prefer to analyze the 6-7.5 τ methoxycarbonyl region of the spectra of styrene-dimethyl itaconate copolymers as shown in Fig. 5. The peak A at low field was assigned to the methoxycarbonyl protons attached to the side chain methylene group. The intervention of the methylene group allows the methyl protons of the methoxycarbonyl to get out of the anisotropic shielding through the phenyl group of the neighboring styrene unit. Peak A simply decreases its intensity as shown in Fig. 4 and does not split. On the other hand, the signal from the methoxycarbonyl attached directly to the polymer backbone split into peaks B, C, . . . in a similar manner as the same group in the styrene-methyl methacrylate copolymer. The side chain methylene group in dimethyl itaconate corresponds to the α-methyl in methyl methacrylate and also shows splitting as the styrene content in copolymer increases. However, the superpositions of peaks prevented the confirmation of this spectral analysis.

Styrene-Methyl Benzyl Itaconate Copolymer

Methyl benzyl itaconate was chosen as M_2 comonomer in place of dimethyl itaconate to simplify the above complications in NMR spectra of styrene-dimethyl itaconate copolymers. Instead of the methyl group of the methoxycarbonyl in dimethyl itaconate, the methylene group of the benzyloxycarbonyl in methyl benzyl itaconate was expected to show its absorption at the 1-2 τ lower position rather than at the former absorption. Then the ambiguity of the assignment of two methoxycarbonyl groups in the dimethyl itaconate unit and the superpositions of the split absorption peaks could be avoided.

The NMR spectrum of polymethyl benzyl itaconate is shown in Fig. 6(a), phenyl protons at 3 τ, benzyl-methylene at 5.3 τ, methoxycarbonyl at 6.7 τ, and two methylenes at 7-8 τ. The two "alkyl" protons of ester groups (one is benzyl-methylene and the other is methyl) show absorptions which are sufficiently separated from each other.

The copolymerization of styrene and methyl benzyl itaconate at 60°C with azobisisobutyronitrile gave $r_1 = 0.42 \pm 0.05$ and $r_2 = 0.19 \pm 0.09$ (95% confidence limit) (Fig. 7). The copolymerization behaviors of dimethyl itaconate and methyl benzyl itaconate are very similar. The monomer reactivity toward the styrene polymer radical ($1/r_1$) of methyl benzyl itaconate is somewhat greater than that of dimethyl itaconate, similar to the relationship between benzyl methacrylate and methyl methacrylate [8].

The NMR spectra of styrene-methyl benzyl itaconate copolymers are shown in Fig. 6(b-j). The spectra are arranged so that the content of styrene increases from (b) to (j). Phenyl protons are not shown for some samples to avoid complication. The interpretation of the spectra is more clear-cut than for styrene-dimethyl itaconate copolymers. The absorptions at 3-4 τ are phenyl protons of both styrene and itaconate units. The peak at low field is assigned to the phenyl protons of the itaconate unit because it appears at the same position as that of itaconate homopolymer and because it decreases its intensity simply from (b) to (j)

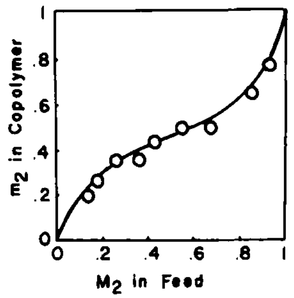


Fig. 7. Copolymerization of styrene (M_1) and methyl benzyl itaconate (M_2); abscissa: M_2 mole fraction in comonomer feed; ordinate: m_2 mole fraction in copolymer.

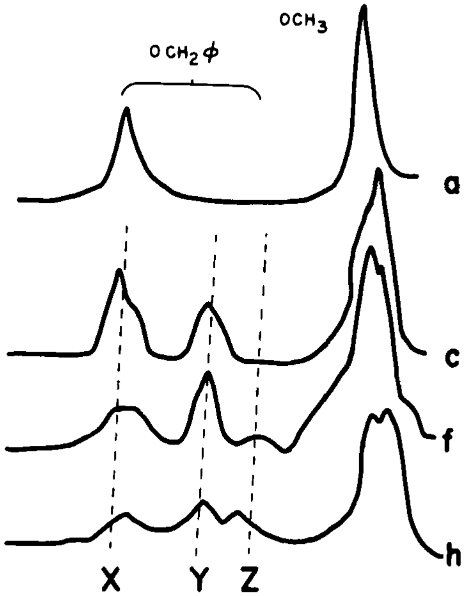


Fig. 8. Split benzyl-methylene proton signals and essentially unsplit methyl proton signals for styrene-methyl benzyl itaconate.

(although minor splitting was observed in some samples). The phenyl protons of the styrene unit appear at 3.4 τ in the (b) spectrum. Its intensity increased with increasing styrene content and a second peak appeared at 3.7 τ. Two peaks at 3.4 and 3.7 τ with 3:2 intensity ratio have been observed for styrene homopolymer [9]. Peaks between 5.3 and 6.3 τ are assigned to the benzyl-methylene protons of the itaconate unit. Details are discussed later. The single peak at 6.7-7 τ with a trivial splitting at the peak top is assigned to the methoxycarbonyl protons of the itaconate unit. The two methylene absorptions between 7 and 8 τ for the itaconate homopolymer gradually shift to a higher magnetic field for copolymers with increasing styrene content, and finally absorptions of the methylene and methine protons of the styrene homopolymer occur at 7.5-9 τ [Fig. 6(k)].

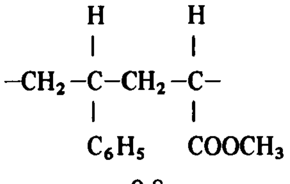
The splitting by benzyl-methylene protons between 5.3 and 6.3 τ can be understood when compared with methoxycarbonyl protons of styrene-methyl methacrylate copolymers. The chemical shift may be roughly grouped into three peaks, X, Y, and Z (Fig. 8). The benzyl-methylene protons in the itaconate unit that is connected with two "co-isotactic" styrene units show absorption at the highest position, Z; those in the itaconate unit that is connected with one "co-isotactic" styrene unit show absorption at the middle position, Y; and those in the itaconate unit without a neighboring "co-isotactic" styrene unit show absorption at X.

The methoxycarbonyl protons show a single peak at 6.7-7 τ, in contrast to the benzyloxycarbonyl protons. The intervention of a methylene group between the methoxycarbonyl group and the polymer backbone allows the methyl protons to escape the anisotropic shielding effect by the neighboring "co-isotactic" styrene unit (Fig. 9).

The determination of "co-isotacticity" σ for the styrene-methyl benzyl itaconate copolymer system was carried out using the following equation proposed by Ito et al. [1]:

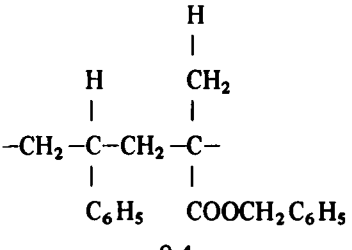
$$1 - F_X^{1/2} = \sigma P_{21} = \sigma/(1 + r_2/x)$$

where $F_X = X/(X + Y + Z)$, i.e., the fraction of the itaconate unit which is connected with no "co-isotactic" styrene unit of the all-itaconate units; $x = [M_1]/[M_2]$, i.e., the styrene-itaconate molar ratio in feed in the copolymerization experiment. The result of such determination is illustrated in Fig. 10. The "co-isotacticity" for the present system is given as ca. 0.5, which is near the value for the styrene-benzyl methacrylate system [1].



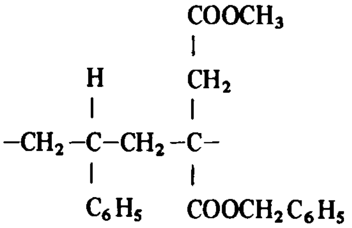
$-CH_2-\overset{H}{\underset{C_6H_5}{C}}-CH_2-\overset{H}{\underset{COOCH_3}{C}}-$

0.8



$-CH_2-\overset{H}{\underset{C_6H_5}{C}}-CH_2-\overset{\overset{H}{|}}{\overset{CH_2}{\underset{COOCH_2C_6H_5}{C}}}-$

0.4



$-CH_2-\overset{H}{\underset{C_6H_5}{C}}-CH_2-\overset{\overset{COOCH_3}{|}}{\overset{CH_2}{\underset{COOCH_2C_6H_5}{C}}}-$

ca. 0.5

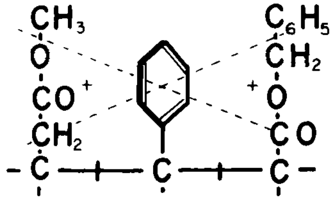


Fig. 9. Anisotropic shielding effect by the neighboring "co-isotactic" styrene unit on the benzyloxycarbonyl and methoxycarbonyl protons of the itaconate unit in the copolymer.

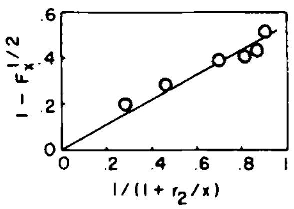


Fig. 10. Determination of "co-isotacticity" for the system of styrene-methyl benzyl itaconate. The spectra (h-j) in Fig. 6 gave split benzyloxycarbonyl proton absorptions that were too weak and so we did not plot them in this determination.

The apparent structural difference between the styrene-methyl benzyl itaconate and the styrene-benzyl methacrylate systems is the substitution of a methoxycarbonyl group for a hydrogen atom of the methyl group in methacrylate. Therefore, it can be concluded that the nonconjugative methoxycarbonyl group of itaconate has little effect on the steric course of the cross-propagation reaction with styrene, although it has an effect on the kinetic course of the cross-propagation reaction.

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