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Determination of Assigned Configurational Parameters for Cross Propagation in Radical Copolymerization of Methyl Methacrylate and Trityl Methacrylate

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Introduction

The compositional and configurational analyses have been described for the copolymer of methyl methacrylate and other methacrylate including trityl methacrylate obtained by radical and anionic initiators (OKAMOTO et al. 1975, YAMADA and TANAKA 1974, YUKI et al. 1978). In these reports the equality was assumed for the two configurational parameters in cross propagation, σ_{12} and σ_{21} or these two parameters were accidentally equal. Here σ_{ij} is the probability of generating a meso dyad when a monomer unit M_j is formed at the M_i end of a growing chain as proposed by BOVEY and TIERS (1963). KLESPER et al. (1969, 1970, 1975) investigated the configurational parameters in the radical copolymers of methyl methacrylate-methacrylic acid, methyl methacrylate-pentadeuteromethacrylic acid and pentadeuterated methyl methacrylate-methacrylic acid, and evaluated the parameters in cross propagation, $\Sigma_s=\sigma_{12}+\sigma_{21}$ and $\Sigma_p=\sigma_{12}\cdot\sigma_{21}$. From their results it was possible to determine the unassigned numerical values for σ_{12} and σ_{21}, but these could not be assigned by their NMR data alone.

In the present work the copolymer of perdeuterated methyl methacrylate (M_1) with a small amount of undeuterated trityl methacrylate (M_2) was radically prepared in tetrahydrofuran and converted into the copolymer of perdeuterated methyl methacrylate with a small amount of undeuterated methyl methacrylate by the selective hydrolysis of the trityl group and subsequent methylation with diazomethane. The ^{1}H NMR spectrum of the derived copolymer allowed to determine the assigned σ_{12} and σ_{21}, which were unequivocally different from each other.

Results and Discussion

The copolymer was prepared in tetrahydrofuran at 60°C with AIBN as an initiator at the ratio of initial monomer concentration, $M_1/M_2=20.6$. The conversion of the monomer to the copolymer was 7.0%. The content of trityl methacrylate unit in the copolymer was found to be 5.0 mol% by the intensity measurement of the ^{1}H NMR

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signal of phenyl protons in the trityl group according to HATADA's procedure (HATADA et al. 1977). In the copolymerization of methyl methacrylate(M_1) and trityl methacrylate(M_2) in tetrahydrofuran at 60°C with AIBN the monomer reactivity ratios, r_1 and r_2, were found to be 0.89 and 0.33, respectively (YAMADA and TANAKA 1974). From these reactivity ratios and the initial monomer ratios the trityl methacrylate content in the initial copolymer obtained here was calculated to be 5.0 mol%, which agreed well with the observed value. This indicates that there is no isotope effect in the monomer reactivity in this copolymerization.

The copolymer was hydrolyzed by refluxing it in methanol containing a small amount of hydrochloric acid for 5hr and the copolymer of perdeuterated methyl methacrylate and methacrylic acid thus obtained was methylated with diazomethane according to the procedure of KATCHALSKY and EISENBERG (1951). The yield through the hydrolysis and methylation was almost 100%. During the hydrolysis procedure only the trityl group was removed as reported in the previous paper (OKAMOTO et al. 1975, YUKI et al. 1975). So the resultant polymer after the methylation should be the copolymer of perdeuterated methyl methacrylate and undeuterated methyl methacrylate, the latter monomer unit came from the trityl methacrylate unit in the original copolymer.

The ^1H NMR spectrum of the derived copolymer is shown in Figure 1A. The spectrum is very similar to that of poly(methyl methacrylate), but it should be noted that the signal comes only from the protons of the undeuterated methyl methacrylate unit distributed sporadically in the whole polymer chain. The three peaks in α-methyl proton region (0.9 ∿ 1.4ppm) should correspond to isotactic, heterotactic and syndiotactic triads with increasing magnetic field, which were centered by trityl methacrylate unit in the original copolymer. Two small peaks at 1.23 and 1.31ppm overlapped with the α-methyl signal were due to the methyl groups introduced into the copolymer from the initiator and were eliminated on the intensity measurement by the peak elimination method (Fig. 1B) (HATADA et al. 1976). The fractions of three M_2 centered triads, $M_1M_2M_1$, $M_2M_2M_1$ and $M_2M_2M_2$ were calculated to be 0.969, 0.031 and 0.000, respectively by using the monomer reactivity ratios mentioned above. Predominant existence of the $M_1M_2M_1$ triad allowed us to approximate the intensities of the α-CH_3 signals due to the isotactic, heterotactic and syndiotactic triads* as follows:

$$I = 0.087 = \sigma_{12}\cdot\sigma_{21} \quad (1)$$
$$H = 0.578 = \sigma_{12}(1-\sigma_{21}) + \sigma_{21}(1-\sigma_{12}) \quad (2)$$
$$S = 0.335 = (1-\sigma_{12})(1-\sigma_{21}) \quad (3).$$

From the equations (1), (2) and (3) the unassigned coisotactic parameters were calculated to be 0.61 and 0.14.

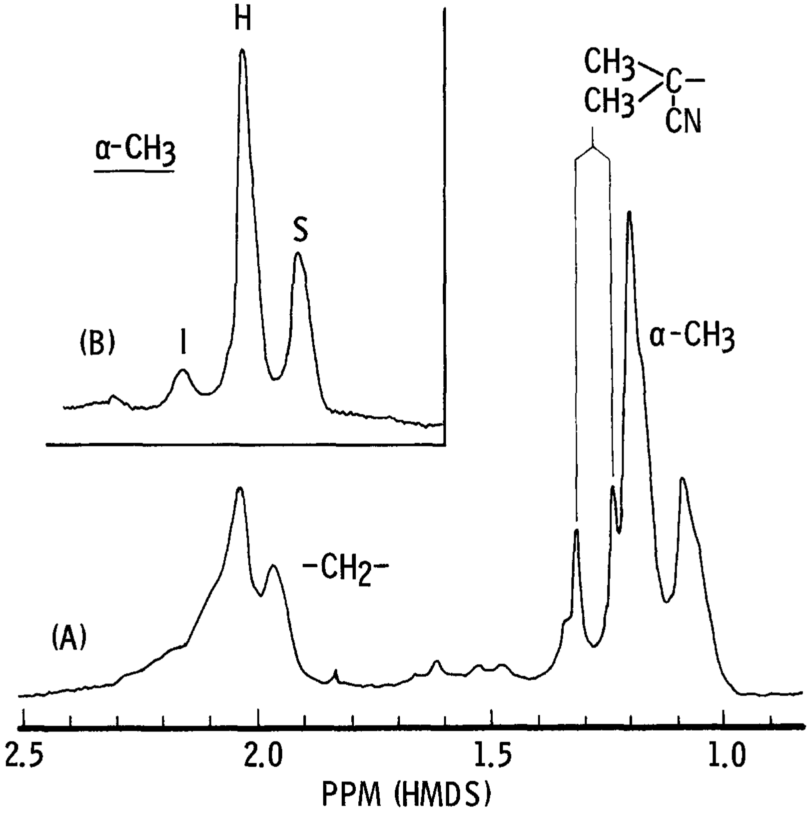

Figure 1. ^{1}H NMR spectra of the copolymer of perdeuterated methyl methacrylate and undeuterated methyl methacrylate derived from the copolymer of perdeuterated methyl methacrylate and trityl methacrylate.
(A) without peak elimination.
(B) with peak elimination.

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* The signals due to the remaining proton (1.18%) in the α-methyl group of the deuterated methyl methacrylate unit overlapped with the α-methyl signals of the undeuterated methyl methacrylate unit. The correction was done for the fraction of the tactic triads by the assumption that the stereoregularity of deuterated methyl methacrylate sequence in the copolymer was the same as that of the homopolymer of perdeuterated methyl methacrylate prepared in tetrahydrofuran with AIBN at 60°C (HATADA).

On the other hand, the resonances in the backbone methylene region should give the information on the value of σ_{12} since the methylene protons belonged originally to the trityl methacrylate unit. Higher intensity of the racemic methylene signal compared with that of the meso methylene one clearly indicate that σ_{12} is smaller than 0.5. Consequently, σ_{12} and σ_{21} should be 0.14 and 0.61, respectively. This clearly indicates that the configurational parameters in cross propagation are different from each other in the radical copolymerization of methyl methacrylate and trityl methacrylate and that the growing chain end of trityl methacrylate unit adds methyl methacrylate in isotactic way while the methyl methacrylate end adds the trityl methacrylate in syndiotactic way. The results show that the structure of the radical end is one of the important factor for the stereoregulation in the propagation reaction. Although most of methacrylates are polymerized to syndiotactic polymer by radical initiator, trityl methacrylate gives isotactic polymer in the radical polymerization even at 60°C (NIEZETTE and RESREUX 1971, YUKI et al. 1968, YUKI et al. 1970). KAMACHI et al. (1978) suggested from their ESR study that the trityl methacrylate radical at the growing chain end in its radical homopolymerization has more rigid conformation than the poly(methyl methacrylate) radical. The results obtained in this study strongly indicate that the trityl methacrylate radical has also rigid conformation which is favorable to isotactic propagation even if it is located alone at the end of fairly long chain of methyl methacrylate. The present work may be the first example of the unequivocal determination of assigned configurational parameters in cross propagation for copolymerization.

Experimental

Perdeuterated methyl methacrylate was prepared from acetone cyanohydrin-d_7 and methanol-d_4 according to the method of CRAWFORD (1934). Trityl methacrylate was synthesized from trityl chloride and silver methacrylate (ADROVA and PROKHOROVA 1961).

Polymerization was carried out in a sealed glass ampoule under nitrogen atmosphere. The reaction mixture was poured into a large amount of methanol and the precipitated polymer was collected by filtration and dried in vacuo at 50°C.

The ^1H NMR spectra were measured in nitrobenzene-d_5 at 110°C on JNM-FX100 Fourier transform NMR spectrometer (JEOL) being operated at 100MHz. Hexamethyldisiloxane was used as an internal standard. The free induction decays were accumulated 100 times.

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Summary

Copolymer of methyl methacrylate-d_8(M_1) with a small amount of trityl methacrylate(M_2) was radically prepared in tetrahydrofuran and converted into the copolymer of methyl methacrylate-d_8 with a small amount of undeuterated methyl methacrylate by the selective hydrolysis of the trityl group and subsequent methylation with diazomethane. From the ^{1}H NMR spectrum of the derived copolymer the assigned coisotactic parameters σ_{12} and σ_{21} were determined to be 0.14 and 0.61, respectively. This may be the first example of the unequivocal determination of assigned configurational parameters in cross propagation for copolymerization.

References

ADROVA, N.A. and PROKHOROVA, L.K.: Vysokomol. Soedin., 3, 1509 (1961)
BOVEY, F.A. and TIERS, G.V.D.: Fortschr. Hochpolym. Forsch., 3, 139 (1963)
CRAWFORD, J.W.C.: B.P. 405,699 (1934)
HATADA, K., OHTA, K., OKAMOTO, Y., KITAYAMA, T., UMEMURA, Y. and YUKI, H.: J. Polym. Sci., Polym. Lett. Ed., 14, 531 (1976)
HATADA, K., TERAWAKI, Y. and OKUDA, H.: Org. Magn. Resonance, 9, 518 (1977)
HATADA, K., KITAYAMA, T., FUJIKAWA, K., OHTA, K. and YUKI, H.: unpublished data
KAMACHI, M., KOHNO M., LIAW, D.-J. and KATSUKI, S.: Polymer J., 10, 69 (1978)
KATCHALSKY, A. and EISENBERG, H.: J. Polym. Sci., 6, 145 (1951)
KLESPER, E. and GRONSKI, W.: J. Polym. Sci., B7, 661 (1969)
KLESPER, E.: J. Polym. Sci., A-1, 8, 1191 (1970)
KLESPER, E., JOHNSEN, A., GRONSKI, W. and WEHRLI, F.W.: Makromol. Chem., 176, 1071 (1975)
NIEZETTE, J. and RESREUX, V: Makromol. Chem., 149, 177 (1971)
OKAMOTO, Y., NAKASHIMA, S., OHTA, K., HATADA, K. and YUKI, H.: J. Polym. Sci., Polym. Lett. Ed., 13, 273 (1975)
YAMADA, A. and TANAKA, J.: Preprints of the 23rd Symposium of Polymer Science, Japan, Tokyo, 1974
YUKI, H., HATADA, K., KIKUCHI, Y. and NIINOMI, T.: J. Polym. Sci., B6, 753 (1968)

YUKI, H., HATADA, K., NIINOMI, T. and KIKUCHI, Y.: Polymer J., 1, 36 (1970)
YUKI, H., OKAMOTO, Y., OHTA, K. and HATADA, K.: J. Polym. Sci., Polym. Chem. Ed., 13, 1161 (1975)
YUKI, H., OKAMOTO, Y., SHIMADA, Y., OHTA, K. and HATADA, K.: J. Polym. Sci., Polym. Chem. Ed., 16, (1978) in press

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