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Conclusions. The present fluorescence data, which overcome the size problem of the previous optical studies, confirm that shear flow may induce mixing on a molecular scale. The flow increases the mutual miscibility of the pair PS/PVME.

The size of composition fluctuations does not collapse abruptly at a critical shear rate, but it is gradually reduced over a range of shear rates. The transition sharpens with increased shearing time, and it moves to lower shear rates. The width of the transition may be attributed to the broad distribution in molecular weight of both polymers and, possibly, to variations in the tacticity of the PVME.

Optical clarity is found to be an indication for mixing on a molecular scale, but it is not a conclusive test. As can be expected, the transition from an opaque to an optically clear blend occurs at a smaller radius (lower shear rate) than the fluorescence quenching transition. Regions of the sample were found to be transparent for white light and, at the same time, strongly fluorescent. In this case, the size of the composition fluctuations simply was below the wavelength of visible light and above the molecular scale.

Our studies are limited to PS/PVME for which the fluorescence quenching phenomenon occurs so conveniently. The method may be extended to other blends by using donor/acceptor tracers[12,13] on the molecules.

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Registry No. PVME, 9003-09-2.

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Observation of Penultimate Effect by ESR of the Model-Propagating Acrylate Radical

The penultimate effect[1] in radical copolymerization has been the subject of considerable debate for a long time in connection with the propagation models such as complex[2] and terminal[3] ones. It is well-known that the copolymerization systems which are reasonably explained by the penultimate model have often contained nitrile monomers as a comonomer.[4] Tirrell and co-workers[5] demonstrated a remarkable reduction of reactivity of the radical bearing a cyano group in a penultimate unit for the attack of acrylonitrile by simple model copolymerization reaction of acrylonitrile and styrene. They explained such reduction by the development in the transition state of dipolar repulsion between cyano groups on the monomer and radical. Recently it has been pointed out by kinetic study that the penultimate model may be a general one applicable to copolymerization systems not involving acrylonitriles such as styrene/methyl methacrylate (MMA)[6] and *p*-chlorostyrene/methyl acrylate[7] systems.

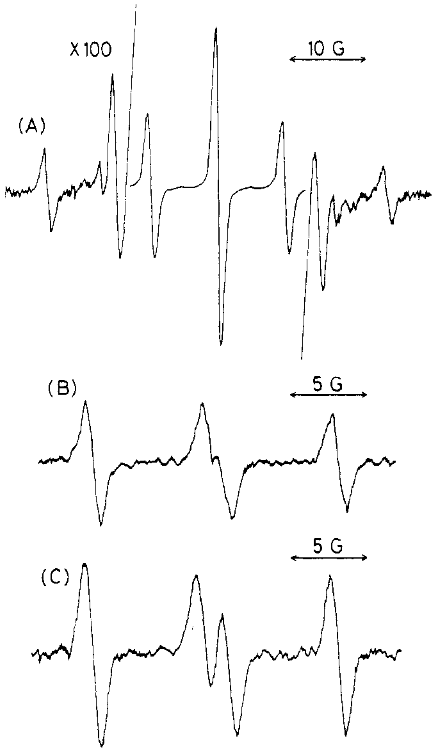
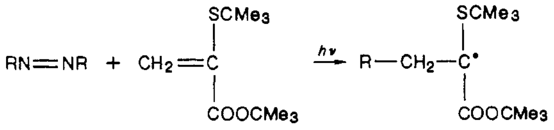


Figure 1. ESR spectra of the radical I in chlorobenzene at 24 °C. (A) R = CMe$_3$, (B) R = Me$_2$CHCH$_2$C(CN)Me, (C) R = Me$_2$C(OMe)CH$_2$C(CN)Me.

Thus far, the debate has been about direct spectroscopic observation of a penultimate effect and the elucidation of its origin. We will demonstrate here that the electronic and conformational structures of a radical itself are indeed sensitive to the nature of the substituent at a penultimate unit and even at a penpenultimate unit by ESR of the model-propagating acrylate radical I.



$$RN{=}NR + CH_2{=}\underset{\displaystyle COOCMe_3}{\overset{\displaystyle SCMe_3}{C}} \xrightarrow{h\nu} R{-}CH_2{-}\underset{\displaystyle COOCMe_3}{\overset{\displaystyle SCMe_3}{C^{\bullet}}}$$

I

Radical I was generated by the photoreaction of *tert*-butyl α-*tert*-butylsulfenylacrylate[8] and corresponding azo compounds in chlorobenzene in an ESR cell under an atmosphere of nitrogen at 24 °C.[9] Figure 1 shows the typical ESR spectra of relatively stable radical I, which gives rise to intense ESR spectra permitting resolution of ^{13}C hyperfine splitting (hfs) in natural abundance presumably because of the captodative substituent effect.[10] In spectrum A (R = CMe$_3$ in radical I), α-^{13}C satellite lines are also observed in the wings of the spectrum as well as the central 1:2:1 triplet due to the splittings by two

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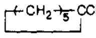
Table I
ESR Parameters of I in Chlorobenzene at 24 °C

	R	hfs constants, G[a]	
		$a_{\beta\text{-H}}$	$a_{^{13}C}$
Ia	Me_3C	8.74	27.1
Ib	$Me_3CCH_2CMe_2$	9.11	27.0
Ic	$Me_2CCOOMe$	8.90	27.1
Id	$Me(CH_2)_{10}$	8.88	*b*
Ie		8.15	26.6
If	Me_2CCN	8.00	26.3
Ig	$MeCH_2C(CN)Me$	7.86, 8.52	25.7
Ih	$Me_2CHCH_2C(CN)Me$	7.68, 8.70	25.9
Ii	$Me_2C(OMe)CH_2C(CN)Me$	7.40, 9.06	*b*

[a] The *a* values were constant within experimental accuracy (±0.15 G). [b] These were not sufficiently intense to resolve ^{13}C hfs in natural abundance.

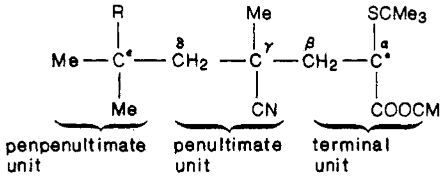
equivalent β-hydrogens. When the substituent R is replaced by a β-cyanoalkyl group, the spectrum is different, as can be seen in spectra B (R = $Me_2CHCH_2C(CN)Me$) and C (R = $Me_2C(OMe)CH_2C(CN)Me$). The intensity of the central line in spectrum B is apparently weakened compared to spectrum A, and in spectrum C a doublet of a doublet is clearly observed.

β-Hydrogen and α-^{13}C satellite hfs constants (*a*) have been measured and are summarized in Table I. It is obvious that the presence of a cyano group in the γ-position, i.e., the α-position of a penultimate unit, of the radical has a tendency to reduce the $a_{\beta\text{-H}}$ and $a_{^{13}C}$ values.[11] Since the $a_{^{13}C}$ value is approximately proportional to the spin density on C_α,[12] a cyano group results in the decrease of the spin density on C_α, and it can be expected that the cyano group in a penultimate unit of a radical leads to retardation of the rate of addition of an electron-accepting olefin to the radical. This is in accord with the kinetic result that an introduction of a cyano group in the γ-position of a propyl radical depresses the relative rate of addition of acrylonitrile by a factor of 3.5.[5] The reactivity of acrylonitrile can be lowered by the decrease of spin density of C_α of a radical itself and probably dipolar repulsion in the transition state.[5,13]

Radicals Ic and If–Ii are models for the propagating species in copolymerization systems of MMA/acrylate and MMA/acrylonitrile, respectively. According to the relation $r_1r_2 = s^2$,[14] where s is k_{211}/k_{111} or k_{122}/k_{222} and k_{pmn} is the rate constant for the radical with a terminal unit m and a penultimate unit p to add a monomer n (p, m, n = 1 or 2), the value of s is calculated to be 0.95, 1.00, and 0.42 for the copolymerization systems of MMA/dodecyl methacrylate,[15] MMA/butyl methacrylate,[15] and MMA/acrylonitrile,[16] respectively, on the basis of their monomer reactivity ratios, r_1 and r_2. A negligible penultimate effect for the former two systems and a considerable one for the latter MMA/acrylonitrile system coincides with the present ESR result on radicals Ia, Ic, and If–Ii; i.e., Ic has similar $a_{\beta\text{-H}}$ and $a_{^{13}C}$ values and hence has similar spin distributions to Ia bearing a simple alkyl substituent in a penultimate unit but If–Ii have different *a* values from Ia and Ic.

A decrease of the $a_{\beta\text{-H}}$ value seems to be attributable not only to the decrease of the spin density on C_α but also to the change of the time-average dihedral angle between the β-hydrogen and the $2p_z$ orbital on C_α. In contrast to Ia–If, Ig–Ii have unequivalent β-hydrogens, and a doublet of a doublet in spectrum C (radical Ii), for example, gradually approached a triplet with increasing temperature. Such variation of spectrum is completely reversible, and hence it is not due to another new radical produced by side reaction. Some long-range coupling[9] between the cyano group and the radical spin on C_α seems to lead somewhat to such a spin distribution and conformational change.

Also noteworthy is the observation of a penpenultimate effect. The difference between ESR spectra B and C, i.e., the radicals Ih and Ii, is due to the methoxy group at the ε-position, i.e., the α-position of a penpenultimate unit as indicated in the following formula:



Ih: R = H
Ii: R = OMe

Bulkiness of the methoxy group would likely affect a mode of interaction between a terminal and a penultimate unit. These remote effects observed may also give a clue to understanding a significant variation of the decomposition rate of azobisnitriles with the substituent at a remote position.[17]

In conclusion, the substituent both at a penultimate unit and a penpenultimate unit of the model-propagating radical influences the spin distribution, i.e., the stabilization,[18] and the conformation of the radical.

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Registry No. Ia, 117499-41-9; Ib, 117499-42-0; Ic, 117499-43-1; Id, 117499-44-2; Ie, 117499-45-3; If, 117499-46-4; Ig, 117526-33-7; Ih, 117526-34-8; Ii, 117526-35-9.

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(12) The $a_{^{13}C}$ value appears to be principally connected with the spin density on C_α, the geometry (planarity) at C_α, and the spin polarization. If the $a_{^{13}C}$ value depends mainly on the planarity and spin polarization, then the $a_{\beta\text{-H}}$ value increases as the size of the R group becomes larger and the $a_{^{13}C}$ value decreases as the R group becomes less electronegative, as indicated by Ingold et al.: Scaiano, J. C.; Ingold, K. U. *J. Phys. Chem.* **1976**, *80*, 275, 1905. The $a_{\beta\text{-H}}$ and $a_{^{13}C}$ values observed in the present study scarcely showed such a tendency. Hence, it is reasonable

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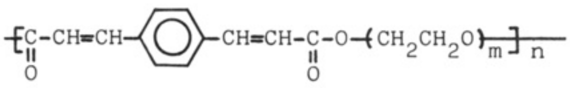
Topochemical Photodimerization in Polymer Liquid Crystals

A topochemical reaction was first demonstrated by Schmidt and co-workers for crystals of cinnamic acid derivatives.[2] The C═C bonds adjacent to the carbonyl group in these compounds dimerize to give cyclobutane rings on photoirradiation with ~300-nm light. The efficiency of the photodimerization was strongly dependent on the structure of crystal forms. In addition, the mode of addition was also influenced by the crystal forms (head-to-head, head-to-tail, and so forth). The idea of topochemical reactions was later developed and applied to photopolymerization by Hasegawa.[3]

If such a topochemical reaction could be applied to polymer systems, two-dimensional reinforced polymer materials might be obtained. For two-dimensional strengthening, biaxial orientation is a possible approach, although it cannot provide polymer materials with ultimate reinforcement. Several attempts have been reported regarding the concept of introducing interpolymer bonding after orientation of the reactive chromophores.[4,5] Bimolecular reaction under restricted molecular motion is a contradicting requirement. Topochemical photoreaction in polymer liquid crystals may allow the formation of two-dimensional reinforced polymer materials.

In Figure 1 the structure of polymers used in this study as well as their abbreviations is shown. *p*-Phenylenediacrylic acid (PDA) and its ethyl ester were synthesized by the method reported previously.[6] Number-averaged molecular weights (M_n) of PE-D and PE-Tr were determined as 7000 (PE-D) and 7200 (PE-Tr) by gel permeation chromatography (GPC) calibrated with standard polystyrene samples. In order to explore the effect of M_n on the photochemical reactivity, the samples of PE-D and PE-Tr were subjected to fractionation by a preparative GPC using chloroform as eluent.



m = 2, PE-D;   m = 3, PE-Tr

Figure 1. Structure and abbreviations of polyesters used in this study.

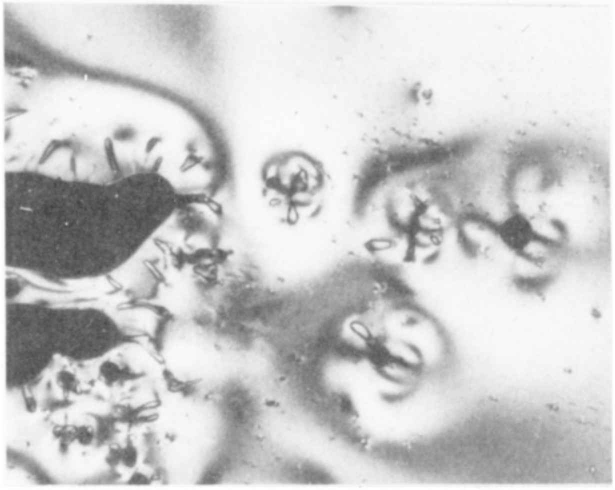


Figure 2. Photograph of texture observed for PE-D under crossed polarizers at 50 °C.

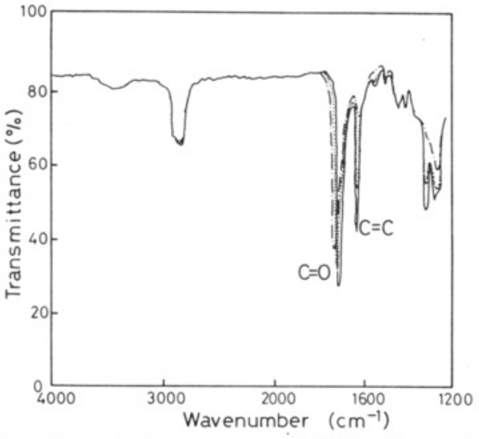


Figure 3. Change in IR spectrum of PE-Tr film on photoirradiation. λ_{ex} = 313 nm: (—) before irradiation; (···) 5 min of irradiation; (-·-) 100 min of irradiation.

Figure 2 shows a typical example of the texture of a polymer film of PE-D observed on a polarizing microscope through a pair of crossed polarizers. The temperature of the sample was controlled within ±0.1 °C with the aid of a Mettler hot stage (FP-80 and FP-82). The texture seen was very similar to that of the schlieren phase, so that PE-D is considered to form a nematic phase. The schlieren-like texture was also observed in the polymer film of PE-Tr, indicating that PE-Tr also forms a nematic phase. Differential scanning calorimetry (DSC) showed that both PE-D and PE-Tr exhibited two endothermic events which corresponded to the glass transition of the polymers (T_g) and to the liquid crystal to isotropic phase transitions (T_{NI}). T_g and T_{NI} of the unfractionated polymers (UF) were T_g = 30 (PE-D) and 14 °C (PE-Tr) and T_{NI} = 87 (PE-D) and 122 °C (PE-Tr). It seems quite reasonable that T_g of PE-Tr is lower than that of PE-D since PE-Tr possessed longer flexible spacers between PDA moieties in the main chain. The higher T_{NI} of PE-Tr may be attributed to the odd-numbered units of spacers between the PDA moieties (odd–even effect).[7]

Unlike low molecular weight liquid crystals, annealing of the polymer films was essential to obtain reproducible results. The polymer films were prepared by casting the polymer solution in chloroform onto glass plates and by evaporating the solvent under reduced pressure. After drying completely, the films were subjected to aging in a thermostat at 70 °C for 5 h. By this procedure, the polymer films always exhibited the same texture as seen

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