Macromolecules **1984**, *17*, 119–120

Scheme I

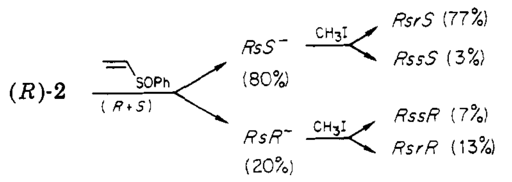

Table I
Stereoelection Observed for the Addition of *rac*-Vinyl Phenyl Sulfoxide to Dimer Anion (*R*)-2

run	$[\alpha]_D$ of 1, deg	[2]/[monomer]	[(*RsS*)-4a]/[(*RsR*)-4a][a]	% dimer[b] in oligomer mixture
1	+194	1	4	
2	0	2.0	12	>97
3	0	1.0	12	>90
4	0	1.0	13	>90

[a] Determined as the 25-MHz ^{13}C intensities of the methyl carbon. [b] Computed from areas under the LC trace of the separated oligomers.

as well as racemic monomer under conditions where virtually only dimeric anion was formed ([2]/[monomer] ≥ 1). Thus, the observed stereoelection represents the true stereoelectivity of 2 toward the monomer enantiomers. The results (Table I) show that the stereoelectivity under these conditions is about 12/1 in favor of the *R*/*S* (or *S*/*R*) addition.

In conclusion, the anionic dimerization of vinyl phenyl sulfoxide according to eq 3 has been demonstrated to occur with very high (>98%) stereoselectivity and high (92%) stereoelectivity. Inspection of Scheme I indicates that methylation of the RsS⁻ dimer anion occurs with considerable stereoselectivity (96%) to produce a carbon of *R* stereochemistry, whereas the corresponding methylation of the RsR⁻ anion is similar but much less stereoselective (65%). Results on the methylation stereochemistry of these anions as well as on the higher oligomers and polymers will be reported in the near future.

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Registry No. (*R*)-**2**, 88180-52-3; (*RsS*)-**4a**, 88180-50-1; (*RsR*)-**4a**, 88243-84-9; (*RsrS*)-**4b**, 88180-51-2; (*RssS*)-**4b**, 88243-85-0; (*RssR*)-**4b**, 88243-86-1; (*RsrR*)-**4b**, 88243-87-2; (±)-CH$_2$=CHS(O)Ph, 88180-53-4.

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(6) The Cahn–Ingold–Prelog convention is used, with upper case letters designating sulfur and lower case letters designating carbon.

(7) Determined by the relative ^{1}H NMR absorptions of the methyl doublets of CD$_3$I methylated **4b**.

Mark A. Buese and Thieo E. Hogen-Esch*
Department of Chemistry, University of Florida
Gainesville, Florida 32611

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Origin of Fluorescence Emission from Poly(vinyl chloride)

Fluorescence spectroscopy has been used in the study of various aspects of several polymers and the subject has been reviewed.[1,2] Although contradictory papers have been reported[3,7], we now believe that the origin of fluorescence emission from polyolefins such as polyethylene and polypropylene can be attributed to polynuclear aromatic (PNA) impurities that are released into the atmosphere in large quantities from the combustion and pyrolysis of fuels and lubricants.[8,9]

Observation of the fluorescence emission of nondegraded poly(vinyl chloride) has been reported, but it has received little attention and the origin of the chromophoric impurities is still unclear.[1,10]

We have now come to the conclusion that the fluorescence species in nondegraded PVC also involve PNA impurities although the intensity of the fluorescence emission is very weak compared to that of the polyolefins.

All samples were commercial products containing no additives. A powdery sample (ca. 30 g) was extracted with 200 mL of an extrapure grade of hexane (Wako Pure Chemical Co. Ltd., Japan) in a Soxhlet extractor for 24 h and then dried under reduced pressure (1 mmHg) for 12 h. Sample films (ca. 0.07 mm thick) of unextracted and extracted high-density polyethylene (HDPE) and isotactic polypropylene (IPP) were prepared by vacuum pressing (see ref 8). Films of unextracted and extracted poly(vinyl chloride) (PVC) were prepared by casting from 1,2-dichloroethane solution and dried under reduced pressure at ambient temperature for 5 h (see ref 11). Fluorescence spectra were recorded with a Hitachi MPF 2A fluorescence spectrophotometer with a xenon source and photomultiplier at room temperature.

In Figure 1, fluorescence emission (λ_{ex} = 240 nm) and excitation (λ_{em} = 340 nm) spectra of PVC are shown in comparison with that of HDPE and IPP. Although the intensity of the spectra of PVC is much weaker than that of HDPE and IPP, the shape of the spectrum is almost same as that of the polyolefins. It shows excitation maxima at ca. 240 and 295 nm and an emission maximum at ca. 340 nm. The results apparently suggest that the origin of chromophoric species in PVC is analogous to that in the polyolefins.

Thus, a fluorescence emission from PVC film prepared from a powdery sample after hexane extraction was observed. As shown in Figure 2, the fluorescence emission observed in the film prepared from the unextracted PVC sample is not found after hexane extraction. However, the extract (hexane solution) shows a fluorescence emission whose shape is similar to that of the unextracted film. In

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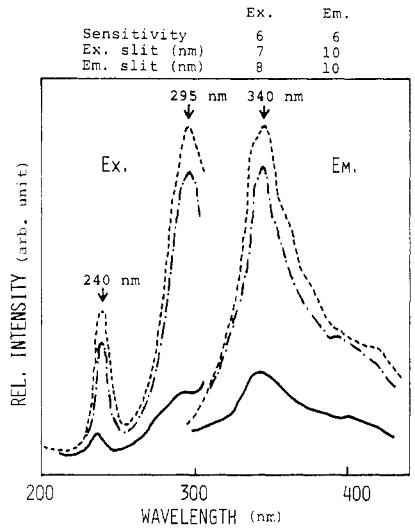

Figure 1. Fluorescence spectra of high-density polyethylene film (- - -), isotactic polypropylene film (–•–), and poly(vinyl chloride) film (—). Uncorrected spectra.

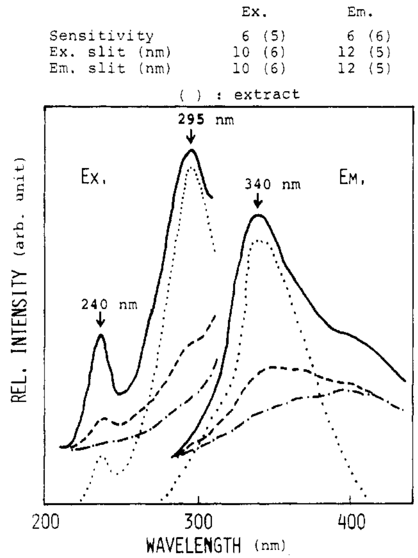

Figure 2. Fluorescence spectra of poly(vinyl chloride): (—) film prepared from an unextracted sample; (–••–) film prepared from an extracted sample after standing for 2 months in an ambient atmosphere; (•••) the extract (hexane solution). Uncorrected spectra.

addition, a broad shoulder observed in the 400-nm region in the unextracted film remains after extraction, but no excitation spectrum corresponding to the 400-nm emission was observed. Therefore, assignment of the shoulder is impossible at present. The results apparently indicate that fluorescence species were extracted from the powdery PVC by hexane and transferred to the hexane.

When a PVC film prepared from the extracted sample showing no fluorescence emission was exposed to the atmosphere for 2 months, a fluorescence spectrum similar to that of the unextracted PVC appeared again. However, the intensity of the spectrum was very weak compared to that of the unextracted film. In the case of HDPE and IPP, the recovery of the intensity of the fluorescence spectra of the extracted film was much faster, reaching that of the unextracted sample after standing ca. 5 h in an ambient atmosphere.[8,9] The differences observed between PVC and polyolefins can probably be ascribed to different affinities of the chromophoric impurities for these polymer.

As mentioned above, the amount of adsorbed chromophoric impurities in PVC was extremely small, but they could be extracted by hexane. In addition, exposure of the extracted PVC film to the atmosphere very slowly formed a fluorescence emission similar to that of unextracted film. Therefore, one can conclude that the fluorescent species in PVC, like those in the polyolefins, are PNA impurities absorbed in the polymer.

Registry No. Poly(vinyl chloride) (homopolymer), 9002-86-2.

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Zenjiro Osawa,* Takashi Takada, and Yutaka Kobayashi

Research Institute of Composite Materials
Faculty of Engineering, Gunma University
Kiryu, Gunma 376, Japan

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Influence of Entanglement on the Dielectric Normal Mode Process of *cis*-Polyisoprene

Linear flexible polymers having dipoles aligned in the direction parallel to the chain backbone exhibit a dielectric relaxation due to fluctuation of the end-to-end distance.[1–3] In dilute solutions of such a polymer, the dielectric relaxation was described by the Rouse–Zimm theory.[4,5] Thus such a relaxation is referred to as "normal mode process". Experimental studies on the normal mode process are relatively rare.[6–11] Among these, Stockmayer and his coworkers studied this subject most extensively.[6–8] Recently, we also reported the dielectric normal mode process in dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide) and found that the dielectric behavior is virtually in accord with the prediction by the Rouse–Zimm theory.[9] However, the data of the normal model process reported to date are concerned mostly with dilute solutions and not at all with the systems in which polymer chains are entangled with one another. It may be expected easily that entanglements cause an increase in the relaxation time as in the case of viscoelastic relaxation time, which has been explained by the tube theory of de Gennes[12] and of Doi and Edwards.[13] In an effort to explore the influence of entanglement on the dielectric normal mode process, we studied dielectric relaxation in undiluted *cis*-polyisoprene (*cis*-PI). In this communication, we report some preliminary results of the study.

Because of the lack of symmetry in the chemical structure of *cis*-PI, this polymer should have nonzero components of dipole moment both parallel and perpendicular to the chain contour. The perpendicular dipole

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