

## Radiation-Induced Polyene Formation of Poly(vinyl Chloride). I. Effect of Conformations

KATSUO MITANI and TAKAYUKI OGATA, *Research & Development Division, Tokuyama Soda Co. Ltd., Mikage-cho, Tokuyama 745, Japan*

### Synopsis

PVC samples with different syndiotacticities were degraded at temperatures in the range of 10° to 115°C by UV radiation. The average length of polyenes increases with increase in syndiotacticity of PVC. It was found that by comparison with the long tactic sequences, on the basis of Bernoullian statistics, the propagation reaction of the polyenes at room temperature is terminated when there are more than three racemic dyads in the tactic sequences. At room temperature, the deformation of about 1.3 Å of the PVC main chain takes place, and at temperatures above the glass transition temperature the propagation rate of the polyenes is competitive with the relaxation time between the (tt) and the (tg) conformations.

### INTRODUCTION

The thermal stability of poly(vinyl chloride) (PVC) as one of the major manufacturing problems has been dealt with quite extensively for some decades. The degradation is a complex one which has been discussed,<sup>1-8</sup> and which can generally be described as a dehydrochlorination which is accompanied by the formation of a series of conjugated double bonds. Only for the dehydrochlorination induced by ultraviolet and high-energy radiation the active centers have been generally recognized as free radicals, and hence the propagation has been accepted to proceed via a free-radical mechanism.<sup>1,9-17</sup>

It is well known that, the radiation-induced dehydrochlorination rate being a linear function of radical production rate, its contribution and the thermal contribution to the composite dehydrochlorination rate should be additive. This indicates the presence of some long-lived species, possibly polyenyl-type stabilized free radicals.<sup>9-11</sup> Nishijima et al.<sup>18</sup> have reported that if the irradiated polymer at liquid nitrogen temperature under vacuum is brought up to 20-150°C, the length of the conjugated double bonds increases with increase in temperature, which increases considerably at temperatures above the glass transition temperature. They have also pointed out that exposure to ultraviolet radiation of the elongated PVC films gives rise to a red shift of the UV absorption bands of the conjugated double bonds.<sup>19,20</sup> Gupta and Pierre<sup>15</sup> have indicated that the highly syndiotactic polymer, having been initiated, has exceedingly long polyene

lengths for degradation. These results suggest that the length of conjugated double bonds can be affected by molecular motion and the conformation of PVC macromolecules since highly syndiotactic polymer and elongated polymer samples are rich in the (tt) conformation which is similar to that of *trans*-polyene.

In this paper, PVC samples with varying syndiotacticity were decomposed by ultraviolet radiation. The mechanism of formation of polyene sequences by dehydrochlorination is discussed based on the tactic data using 100-MHz and 220-MHz NMR spectra. The longer tactic sequences, more than three, are interpreted on the assumption of Bernoullian statistics. Furthermore, the mechanism of formation of polyene sequences is discussed from the viewpoint of the molecular motion of the PVC chain.

## EXPERIMENTAL

PVC samples were prepared at a selected temperature in the range from 40° to -78°C using the triethylboron-oxygen catalyst system. The polymers obtained were purified by the usual method.

Proton NMR spectra were obtained on 5-10% solutions of PVC in *o*-dichlorobenzene at 165°C, and recorded with Varian HR-220 and JOEL-4H-100 spectrometers. Hexamethylsiloxane (1%) was used as internal reference standard.

Infrared spectra were obtained on cast films of PVC by using a Hitachi EPI-G3 spectrometer.

Thermogravimetry was performed in a vertical tubular oven in air using Rigaku Denki differential thermal analysis equipment. The samples, 15 mg each, were contained in shallow platinum dishes, and the sample weight was monitored with an electrobalance and continuously recorded. The heating rate was 10°C/min.

Cyclohexanone solution of PVC was cast on a glass plate followed by washing with boiling methanol. PVC films, 50-70  $\mu$  thick, were dried at 40°C for one day. Films contained in evacuated thin-walled quartz cell unit windows which were heated or cooled externally to  $\pm 1^\circ\text{C}$  were irradiated with light from a Toshiba Type SHL-100, low-pressure, compact-source mercury arc. The distance between light source and sample was 4 cm. Absorbance of the films was measured in a Hitachi Type 323 spectrometer.

## RESULTS AND DISCUSSION

### Characterization of PVC

It is well known that the trialkylboron-oxygen catalyst system is effective for the polymerization of vinyl chloride, and that vinyl chloride polymerizes by a free-radical mechanism under the action of this catalytic system.<sup>22-27</sup> As Table I shows, the triethylboron-oxygen catalyst system has a high

activity in the polymerization of vinyl chloride. The glass transition temperature ( $T_g$ ) of PVC increases with decrease in polymerization temperature. The increase in  $T_g$  has been attributed to the increase of stereoregularity and the decrease of branching.<sup>28-31</sup> If the configuration of the growing polymer is described by Bernoullian statistics, the relation among  $I$ ,  $H$ , and  $S$ , the probabilities of forming isotactic, heterotactic, and syndiotactic triads, must be represented by eq. (1):

$$4IS/H^2 = 1. \quad (1)$$

As shown in Table I, the values calculated from eq. (1) are very nearly unity. This evidence suggests also that polymerization of vinyl chloride with the triethylboron-oxygen catalyst system proceeds by a free-radical mechanism.

Thermogravimetry of PVC samples programmed at a heating rate of 10°C/min in air atmosphere is illustrated in Figure 1. On heating to temperatures in excess of 200°C, a first-stage weight loss of about 2-4% is observed, but was not determined quantitatively because of some scatter of the baseline. Major loss ensues above 260°C, corresponding to the evolution of hydrogen chloride. The decomposition temperature increases with decrease in polymerization temperature. The sites for the initiation reaction have been assumed to be the inherent weak links in the polymer chain, such as tertiary chloride<sup>5,31</sup> and allyl chloride adjacent to a carbon-carbon double bond.<sup>1,5,32,33</sup> Therefore, as was done earlier by other investigators,<sup>5,15,30,31</sup> this result suggests that the polymer prepared at low temperature has fewer branch points as the source of degradation initiation.

TABLE I  
Analysis of PVC Obtained by Triethylboron-oxygen Catalyst

Sample	Polymer temp., °C	Polymer time, min	Conversion, %	$M_w^a$ $\times 10^{-4}$	$T_g^b$ , °C	Dyad <sub>sc</sub>	Triad <sup>d</sup>			4IS/H <sup>2</sup>
							<i>I</i>	<i>H</i>	<i>S</i>	
S1	40	60	15.9	2.8	78	0.58	0.18	0.48	0.34	1.0
S2	20	90	12.5	3.2	80	0.60	0.17	0.48	0.35	1.1
S3	0	120	9.7	4.9	82	0.62	0.15	0.47	0.38	1.1
S4	-40	150	7.8	3.9	87	0.67	0.12	0.45	0.43	1.0
S5 <sup>e</sup>	-78	180	5.2	—	—	0.71	0.09	0.42	0.49	1.0

<sup>a</sup> All polymerization runs were carried out by using 150-ml glass ampoules. After 0.5 mmole triethylboron and oxygen were added to 20 ml *n*-heptane at -78°C under nitrogen atmosphere, 20 g vinyl chloride was introduced and the ampoule was kept at a chosen temperature. The molecular weight of PVC was determined by Nakazawa's equation<sup>21</sup>:  $[\eta] = 1.42 \times 10^{-4} M_w^{0.82}$  at 30°C in cyclohexanone solution.

<sup>b</sup> Obtained from DSC.

<sup>c</sup> Syndiotactic dyad (*s*) placements were obtained from 100-MHz NMR spectra.

<sup>d</sup> Obtained from 220-MHz NMR spectra.

<sup>e</sup> Sample S5 was insoluble in cyclohexanone.

### Ultraviolet Irradiation of PVC

Figure 2 shows the UV spectra of PVC samples which were decomposed at 105°C under vacuum by ultraviolet radiation. These spectra adequately account for the constancy of polyene distribution during the early stages of radiation-induced dehydrochlorination. In thermal, ultraviolet-induced, and high energy-induced degradation of PVC, the macromolecules mainly undergo chain scission, crosslinking, and formation of polyene

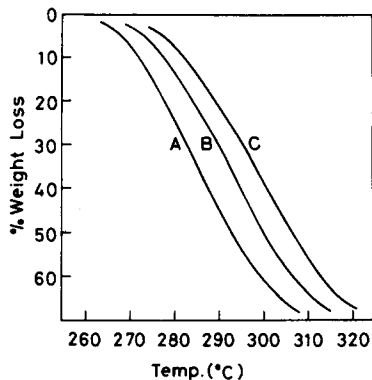


Fig. 1. Thermogravimetry of PVC samples: (A) sample S1; (B) sample S4; (C) sample S5.

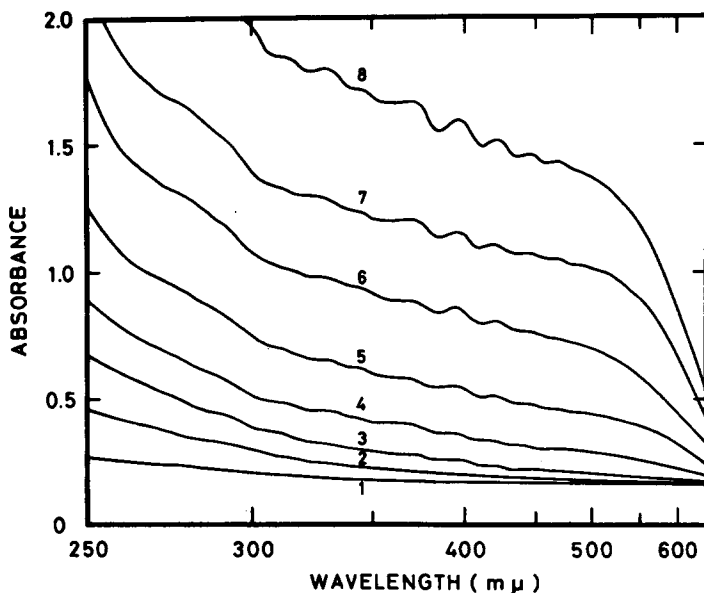


Fig. 2. Spectra of sample S1 degraded at 105°C by ultraviolet irradiation. Irradiation time: (1) 0; (2) 5 min; (3) 10 min; (4) 18 min; (5) 35 min; (6) 60 min; (7) 85 min; (8) 120 min.

sequences by dehydrochlorination; the relative extent of these reactions depends on the experimental conditions. In this regard, it should be mentioned that no change in molecular weight has been revealed by cloud-point measurements of the samples degraded by ultraviolet radiation (Fig. 3). At the early stage, therefore, other reactions such as crosslinking and chain scissions cannot conceivably play any major role in the mild degradation conditions of this work. Ultraviolet radiation mainly results in the dehydrochlorination of PVC which is accompanied by the formation of a series of conjugated double bonds.

It may be assumed, as was done earlier by other investigators,<sup>17,34-36</sup> that the spectrum of degraded PVC in the ultraviolet and shortwave part of the visible region contains 10 to 13 not very well-defined maxima, assignable to polyene segments of different lengths and which appear in the polymer molecules as a result of the elimination of hydrogen chloride. The spectrum of PVC degraded by ultraviolet radiation under vacuum, shown in Figure 1, is typical, and the maxima in the longwave region are listed in Table II together with the absorption coefficient at each wavelength. For the assessment of the  $n$  values to wavelengths of the maxima in the spectrum, over which there is some controversy, a convenient reasoning should be considered that has already been proposed by some workers.<sup>34-36</sup> The wavelengths of these peaks can be conveniently taken from the data found by Sondheimer et al.<sup>34</sup> for a number of low polyene homologs. As shown in Figure 4, there is a good linearity between the length of polyene sequences,  $n = 4-10$ , and their absorption coefficients. By extrapolation of this plot to long polyenes, the absorption coefficients for  $n = 11-13$  were determined (Table II). Although with a still higher degree of arbitrariness, the degraded PVC spectrum is also susceptible to quantitative analysis.

As given in Table II, the extinction coefficients of polyenes increase as the length of the conjugated sequence increases. Therefore, short polyenes predominate in degraded PVC, and the greater the length of polyene, the small is its fraction in the total conjugated structure. From Figure 1, it is

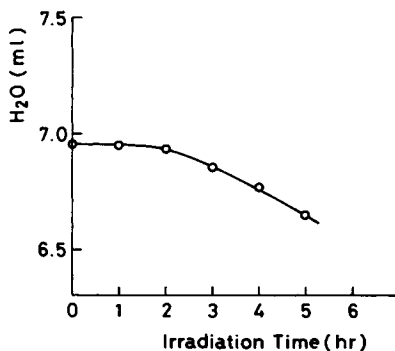


Fig. 3. Clouding points of sample S1 degraded at 105°C. Sample S1 (130 mg) was dissolved in 50 ml tetrahydrofuran and the solution was titrated with H<sub>2</sub>O.

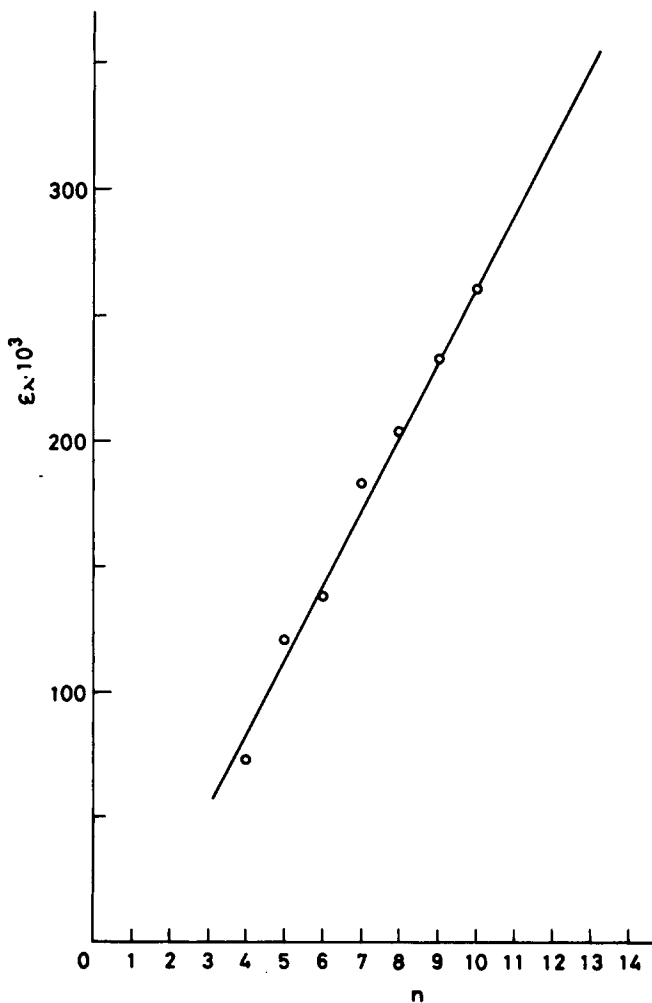


Fig. 4. Relation of molar absorption coefficient of polyenes to polyene length  $n$ .<sup>34</sup>

impossible to determine the content of polyenes with sequences of more than 14 double bonds, since the wavelength of the maxima in their polyene sequences is indistinguishable in the spectrum. On the basis of the method proposed by Kelen et al.,<sup>37,38</sup> the average length of polyenes can be calculated. Figure 5 shows the logarithmic concentrations of polyenes versus their lengths, and, with sequences of more than five double bonds, gives a straight line whose slope allows calculation of the average polyene length:

$$\log C_i \alpha (i - 1) \log k \quad (2)$$

$$\bar{n} = 1/k \quad (3)$$

where  $C_i$  is the concentration of an  $i$ -long polyene,  $k$  is the propagation probability of polyene, and  $\bar{n}$  is the average length of polyene.

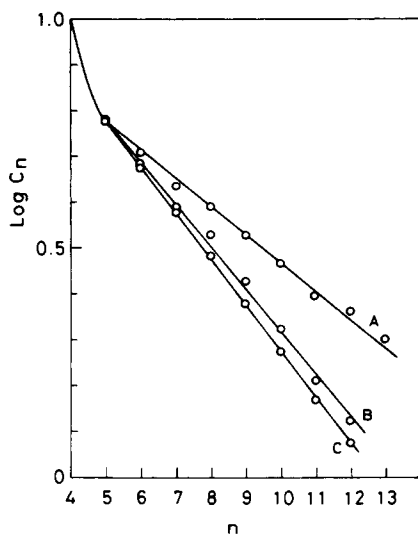


Fig. 5. Logarithmic concentrations of polyenes  $C_n$ , vs. their length  $n$  (sample S1). Irradiation temperature: (A) 105°C; (B) 50°C; (C) 10°C. It was assumed that  $\log C_4$  equals 1.0.

TABLE II  
Molar Absorption Coefficient of Polyenes

$n^a$	Wavelength, <sup>b</sup> $m\mu$	Molar absorption coefficient $\epsilon_\lambda \times 10^3$ <sup>c</sup>
4	312	73
5	329	121
6	345	138
7	371	174
8	395	204
9	421	233
10	445	261
11	467	292
12	485	320
13	515	348

<sup>a</sup> Number of conjugated double bonds.

<sup>b</sup> Strongest absorption.

<sup>c</sup> Estimated values based on the data of Sondheimer.<sup>34</sup>

Figure 6 shows the average polyene length versus radiation temperature. The average polyene length increases with increase in syndiotacticity. The linear high syndiotactic polymers do not initiate chain formation easily, but, once initiated, they have exceedingly long chain lengths for their decomposition.

### Polyene Distribution and PVC Conformations

As shown in Figure 7, the infrared spectra of the radiation-induced degraded PVC samples give absorption bands of *trans*-polyene and double

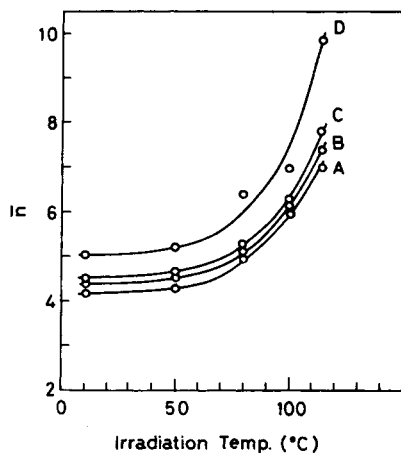


Fig. 6. Plot of average polyene length vs. irradiation temperature: (A) sample S1; (B) sample S2; (C) sample S3; (D) sample S4.

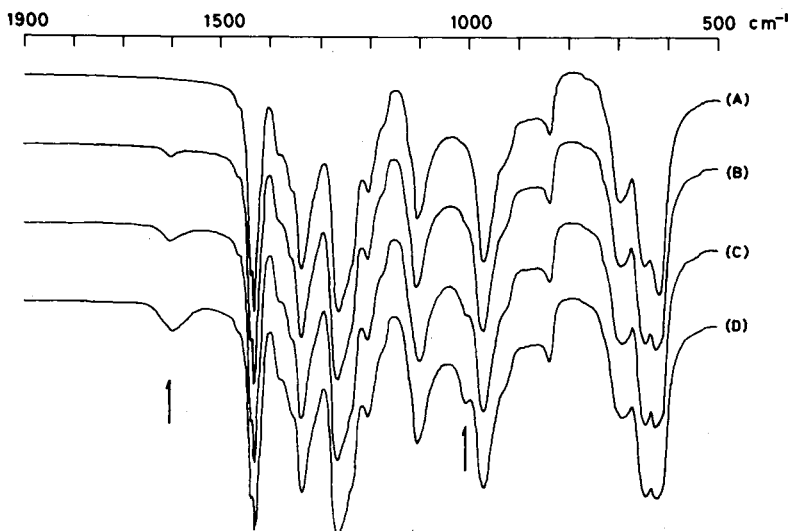
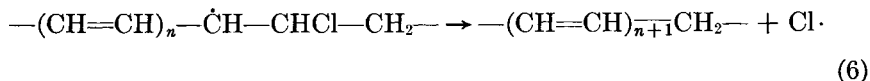
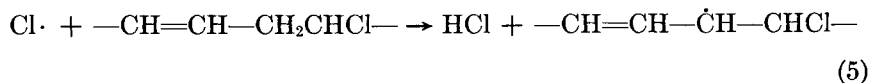
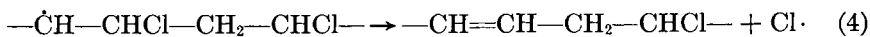


Fig. 7. Infrared spectra of sample S4 degraded at 105°C under vacuum by ultraviolet radiation. Irradiation time: (A) 0; (B) 3 hr; (C) 6 hr; (D) 12 hr.

bonds, at  $1010\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , respectively, and not of *cis*-polyene. This evidence conflicts with Iwami's data<sup>39</sup> that thermally degraded PVC powder gives *cis*-polyene. This conflicting evidence suggests that the mechanism of the hydrogen chloride elimination from PVC in thermal degradations differs from that in radiation-induced degradations. From dehydrochlorination results reported in the literature, it is not yet possible to make a choice between molecular elimination and radical-chain process for PVC degradation. However, the formation of long conjugated un-



saturated sequences from irradiated PVC has been accounted for by a radical-chain mechanism due to presence of polyenyl and free radicals<sup>9-13</sup>.



This reaction scheme adequately accounts for the constancy of polyene distribution during the early stages of radiation-induced dehydrochlorination.

From the NMR spectra of PVC, several authors<sup>40-43</sup> have concluded that in the meso dyad, the (tg) and (gt) conformations occur in the sequences ... (tg)(tg) ..., ... (gt)(gt) ..., or ... (gt)(tg) ..., while in the racemic dyad, essentially only the (tt) conformation is allowed because of a large electrostatic repulsion between chlorine atoms in the (gg) form. The (tt) form is very similar to the *trans*-polyene structure. Nishijima et al.<sup>19,20</sup> have reported that the uniaxially oriented PVC film, enriched in the (tt) conformation by elongation, gives long polyenes by radiation-induced decomposition. This evidence may suggest that the formation of the *trans*-polyene from the (tt) conformation is very easy without any change in the PVC chain, but that the formation *trans*-polyene from the (tg) and (gt) conformations is difficult because of the large deformation of the C-C bond in the main chain (Fig. 8). The propagation reaction of polyene expressed in eq. (6) closely relates to the conformation of the PVC chain, i.e., the propagation rate of the *trans*-polyene from the (tt) conformation in the

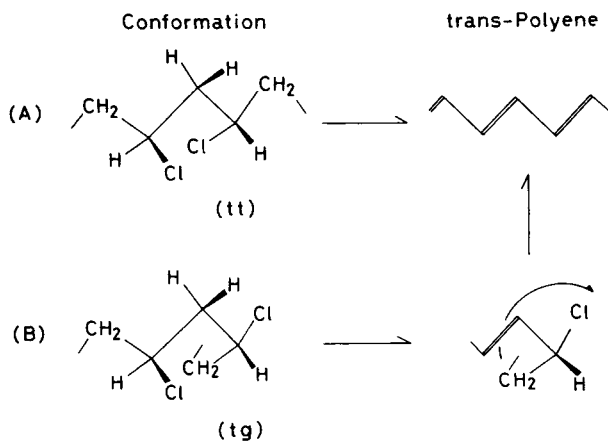


Fig. 8. Diagram of formation of *trans*-polyene from the (tt) and (tg) conformations in the PVC chain. Arrows ( $\rightarrow$ ) and ( $\curvearrowright$ ) indicate propagation reaction of polyenes and deformation of the C-C bond, respectively.

PVC chain is much larger than the termination rate, but in the (tg) or (gt) conformation, the latter becomes larger than the former.

Then the assumption was made that the propagation of *trans*-polyene occurs at temperatures below  $T_g$ , at which the molecular motion of the PVC main chain is frozen, only from the (tt) conformation. In such a case, the fraction of a  $k$ -long polyene can be expressed as follows:

$$P_k = P_s^k P_i \quad (7)$$

where  $P_s$  and  $P_i$  are the probabilities of forming syndiotactic and isotactic dyads, respectively. Thus, plotting the logarithms of the polyene fractions against their lengths  $k$  gives a straight line whose slope allows calculation of the average polyene length  $\bar{n}$ :

$$\bar{n} = 1/P_i \quad (8)$$

The average polyene lengths of sample S1, S2, S3, and S4 calculated using eq. (8) are 2.5, 2.6, 2.7, and 3.1, respectively. These values are much smaller than those below  $T_g$ , shown in Figure 6. This result suggests that propagation of polyene occurs not only from syndiotactic sequences (tt conformations), but also from a few isotactic sequences (tg conformations); and even below  $T_g$  the molecular relaxation between the (tt) and (tg) conformations is allowed to some extent. The concentration of a  $k$ -long polyene was expressed as a function of the number of the (tg) conformations on the basis of Bernoullian statistics. The results are listed in Table III. Figure 9 shows the theoretical plots of the logarithmic polyene concentration versus their length  $n$  as a function of the number of meso dyads (tg

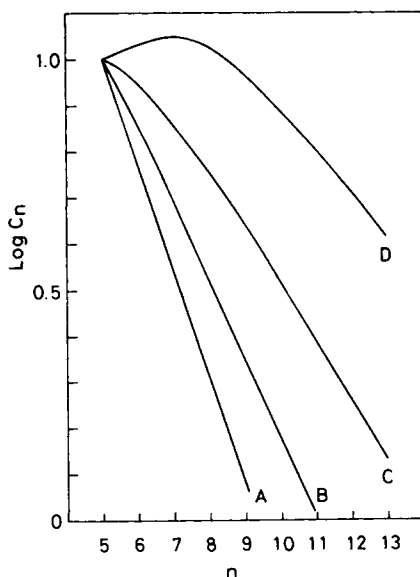


Fig. 9. Theoretical plots of logarithmic polyene concentrations  $\log C_n$  vs. polyene length  $n$  (sample S1). Number of meso dyads (tg conformations)  $x$ : (A)  $x = 0$ ; (B)  $x = 1$ ; (C)  $x = 2$ ; (D)  $x = 3$ . It was assumed that  $\log C_5$  equals 1.0.

conformations),  $x$ . These plots do not give good straight lines except for  $x = 0$ . The average polyene length was obtained from the average slope between  $n = 7$  and  $n = 12$ . The results are given in Table IV. By comparison with the experimental data in Figure 6 at temperatures below  $T_g$ , it has become apparent that the propagation of the *trans*-polyene is terminated if there are more than three meso dyads (tg conformations) in a chain. The formation of the *trans*-polyene sequence from two meso dyads (tg conformations) in a chain, either two meso dyads are isolated or groups in a macromolecular chain, requires the deformation (ca. 1.3 Å) of the carbon atoms in the chain backbone about an axis in the plane and perpendicular to the chain. This evidence thus suggests that the molecular motion of about 1.3 Å of PVC chain is allowed at temperatures in the range from 10 to 50°C below  $T_g$ .

Figure 10 shows the UV absorption spectra of the conjugated double bonds as the irradiation temperature was maintained at 50°C during the first 2.0 hr and finally was raised to 105°C for 1.0 hr. The absorbance at long wavelengths increases considerably at a temperature above  $T_g$ . This is in accord with Nishijima's data<sup>18</sup> that the concentrations of polyenes more than ten increases considerably at temperatures above  $T_g$ . No absorption of conjugated double bonds was observed for PVC heated under vacuum at 105°C for 5 hr. As shown in Figure 6, the considerable increase in average length of polyenes at temperatures above  $T_g$  can be as-

TABLE III  
Relation of Fraction of Polyenes to Number of Meso Dyads in a Tactic Sequence

$n^a$	Fraction of polyenes <sup>b</sup>			
	$x = 0$	$x = 1$	$x = 2$	$x = 3$
5	$P_s^5P_i$	$5P_s^4P_i^2$	$10P_s^3P_i^3$	$10P_s^2P_i^4$
6	$P_s^6P_i$	$6P_s^5P_i^2$	$15P_s^4P_i^3$	$20P_s^3P_i^4$
7	$P_s^7P_i$	$7P_s^6P_i^2$	$21P_s^5P_i^3$	$35P_s^4P_i^4$
8	$P_s^8P_i$	$8P_s^7P_i^2$	$28P_s^6P_i^3$	$56P_s^5P_i^4$
9	$P_s^9P_i$	$9P_s^8P_i^2$	$36P_s^7P_i^3$	$84P_s^6P_i^4$
10	$P_s^{10}P_i$	$10P_s^9P_i^2$	$45P_s^8P_i^3$	$120P_s^7P_i^4$
11	$P_s^{11}P_i$	$11P_s^{10}P_i^2$	$55P_s^9P_i^3$	$165P_s^8P_i^4$
12	$P_s^{12}P_i$	$12P_s^{11}P_i^2$	$66P_s^{10}P_i^3$	$220P_s^9P_i^4$

<sup>a</sup> Length of polyenes.

<sup>b</sup> Number of meso dyads (tg conformations).

TABLE IV  
Average Polyene Length of PVC Samples

Sample	$\bar{n}^a$	Average length of polyenes			
		$x = 0$	$x = 1$	$x = 2$	$x = 3$
S1	4.3	2.5	3.0	4.2	6.0
S2	4.4	2.6	3.2	4.3	6.9
S3	4.6	2.7	3.4	4.7	9.3
S4	5.2	3.1	3.7	5.4	12.0

<sup>a</sup> Obtained from UV spectra at 50°C (Fig. 6).

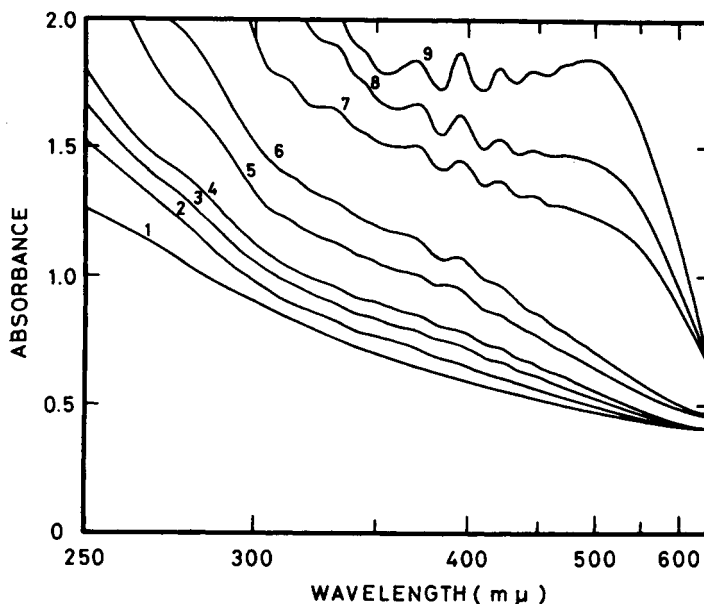


Fig. 10. Absorbance of sample S5 (in the form of molded block) degraded at 50°C for 120 min: (1) 0 min; (2) 15 min; (3) 30 min; (4) 45 min; (5) 90 min; (6) 120 min, and at 105°C for 60 min: (7) 20 min; (8) 40 min; (9) 60 min.

ascribed to a free rotation of the chain backbone of PVC, i.e., the relaxation of the PVC conformations makes easy the propagation reaction of the long polyenes. In addition, the evidence that even at temperatures above  $T_g$  the average length of polyenes of highly syndiotactic PVC is longer than that of PVC with low syndiotacticity indicates that the propagation rate of polyenes is competitive with the relaxation time between the (tt) and (tg) conformations in the PVC chain.

## CONCLUSIONS

UV-irradiated PVC forms *trans*-polyene which arises predominantly from the (tt) conformation in the PVC chain. The average polyene length becomes longer as the syndiotacticity of PVC increases. By comparison with the tactic sequences of PVC on the basis of Bernoullian statistics, it has become apparent that the propagation of the conjugated double bonds is able to proceed beyond two (tg) conformations in the backbone, and molecular motion of about 1.3 Å in the main chain is allowed below  $T_g$ . At temperatures above  $T_g$  of PVC, the propagation rate of the polyenes is competitive with the relaxation time of the (tt  $\rightleftharpoons$  tg) conformation.

## References

1. E. J. Arlman, *J. Polym. Sci.*, **12**, 543, 547 (1954).
2. K. H. Wartman, *Ind. Eng. Chem.*, **47**, 1013 (1955).
3. B. Baum and L. H. Wartman, *J. Polym. Sci.*, **28**, 537 (1958).
4. D. E. Winkler, *J. Polym. Sci.*, **35**, 3 (1959).

5. W. I. Bengough and H. M. Sharp, *Makromol. Chem.*, **66**, 31 (1963).
6. M. Ashahina and M. Onozuka, *J. Polym. Sci. A*, **2**, 3305, 3315 (1964).
7. Z. V. Popova, N. V. Tikhova, and G. A. Razuvaev, *Vysokomol. Soydin.*, **7**, 731 (1965).
8. W. C. Geddes, *Eur. Polym. J.*, **3**, 267 (1967).
9. A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).
10. E. J. Lawton and J. S. Balwit, *J. Phys. Chem.*, **65**, 815 (1961).
11. G. J. Atchison, *J. Polym. Sci.*, **49**, 385 (1961).
12. R. Salovey, J. P. Luongo, and W. A. Yeager, *Macromolecules*, **2**, 198 (1969).
13. R. Salovey and H. E. Blair, *J. Appl. Polym. Sci.*, **14**, 713 (1970).
14. G. Palma and M. Carenza, *J. Appl. Polym. Sci.*, **14**, 1737 (1970).
15. V. P. Gupta and L. E. ST. Pierre, *J. Polym. Sci. A-1*, **8**, 37 (1970).
16. R. Salovey and R. C. Gebauer, *J. Polym. Sci. A-1*, **10**, 1533 (1972).
17. G. Palma and M. Carenza, *J. Appl. Polym. Sci.*, **16**, 2485 (1972).
18. Y. Nishijima, M. Yamamoto, and M. Yano, *Kogyo Kagaku Zasshi, Japan*, **72**, 276 (1969).
19. O. Kyoda, M. Yano, and M. Yamamoto, and Y. Nishijima, *Rep. Progr. Polym. Phys., Japan*, **12**, 497 (1969).
20. M. Yano, M. Yamamoto, and Y. Nishijima, Symposium of Chemical Industry of PVC, *The Society of Polymer Science*, Osaka, Japan, 1970, p. 16.
21. A. Nakazawa, T. Matsuo, and H. Inagaki, *Rep. Progr. Polym. Phys., Japan*, **10**, 67 (1967).
22. N. Ashikari and N. Nishimura, *J. Polym. Sci.*, **28**, 227 (1958).
23. J. W. L. Fordham and C. L. Sturm, *J. Polym. Sci.*, **33**, 503 (1958).
24. J. Furukawa, T. Tsuruta, T. Imada, and H. Fukutani, *Makromol. Chem.*, **31**, 122 (1959).
25. N. L. Zutty and F. J. Welch, *J. Polym. Sci.*, **43**, 445 (1960).
26. S. Inoue, T. Tsuruta, and J. Furukawa, *Makromol. Chem.*, **40**, 13 (1961).
27. F. S. Arimoto, *J. Polym. Sci. A-1*, **4**, 275 (1966).
28. J. W. L. Fordham, *J. Polym. Sci. A-1*, **39**, 321 (1959).
29. S. Krimm, A. R. Berens, V. L. Folt, and J. J. Shipman, *Chem. Ind.*, 1512 (1958); *ibid.*, 433 (1959).
30. A. Nakajima, H. Hamada, and S. Hayashi, *Makromol. Chem.*, **95**, 40 (1966).
31. A. Rigo, G. Palma, and G. Talamini, *Makromol. Chem.*, **153**, 219 (1972).
32. G. Talamini and G. Pezzin, *Makromol. Chem.*, **39**, 26 (1960).
33. A. Crosato-Arnaldi, G. Palma, E. Peggion, and G. Talamini, *J. Appl. Polym. Sci.*, **8**, 747 (1964).
34. F. Sondheimer, D. A. Ben-Efrain, and R. Wolovsky, *J. Amer. Chem. Soc.*, **83**, 1675 (1961).
35. W. I. Bengough and T. K. Varma, *Eur. Polym. J.*, **2**, 61 (1966).
36. Y. Shindo and T. Hirai, *Makromol. Chem.*, **155**, 1 (1972).
37. T. Kelen, G. Báliant, G. Galambos, and T. Tüdös, *Eur. Polym. J.*, **5**, 597 (1969).
38. T. Kelen, G. Galambos, F. Tüdös, and G. Báliant, *Eur. Polym. J.*, **6**, 127 (1970).
39. Y. Iwami, H. Ishikawa, and Y. Minoura, *Kogyo Kagaku Zasshi, Japan*, **72**, 2478 (1969).
40. T. Shimanouchi, M. Tasumi, and Y. Abe, *Makromol. Chem.*, **86**, 43, (1965).
41. Y. Abe, M. Tasumi, T. Shimanouchi, S. Satoh, and R. Chüjô, *J. Polym. Sci. A-1*, **4**, 1413 (1966).
42. F. Heatley and F. A. Bovey, *Macromolecules*, **2**, 241 (1969).

Received March 25, 1974

Revised April 30, 1974