Sequence Distribution in 1-Chloro-1,3-butadiene: Styrene Copolymers[1]

A. Winston* and P. Wichacheewa

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506.

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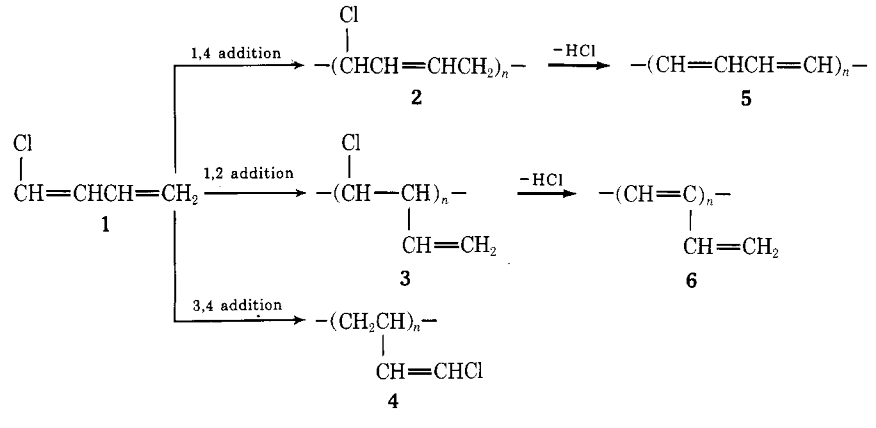
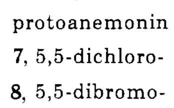
ABSTRACT: The monomer, 1-chloro-1,3-butadiene (M_2) (1), readily copolymerizes with styrene (M_1) under the influence of γ rays from cobalt-60. The copolymer compositions at various feeds were determined from carbon and chlorine analyses. The reactivity ratios were found to be $r_1 = 0.23 \pm 0.02$ and $r_2 = 1.02 \pm 0.10$. On heating, or on treatment with triethylamine in dimethylformamide, the copolymers readily lose HCl to form sequences of conjugated olefinic structural units. The ease of elimination of HCl by the copolymers and the high reactivity of 1-chloro-1,3-butadiene, as indicated by the reactivity ratios, is consistent only with a 1,4-addition polymerization process to give -($CHClCH{=}CHCH_2$)- (2) structures. Ir and nmr data also support this interpretation. After elimination, the copolymers exhibit a number of intense bands in the ultraviolet spectra. These bands may be arranged in sets, where the bands within each set retain the same relative intensities regardless of the composition of the copolymer: set 1 (298, 312, 327 nm), set 2 (347, 367, 388 nm), set 3 (412, 437 nm), and set 4 (473 nm). These sets of bands were assigned respectively to conjugated polyene sequences of the structure -$(CH{=}CHCH{=}CH)_n$- (3), where n = 2, 3, 4, and 5. The relative intensities of the sets change with changing 1-chloro-1,3-butadiene content in the feed exactly as would be expected on the basis of the changing sequence distribution. The distribution of 1-chloro-1,3-butadiene sequences for each of the copolymers was calculated from the reactivity ratios and the appropriate feed compositions. These data were used to obtain the sequence ratios, defined as %n sequences/%(n + 1) sequences. From the ultraviolet spectrum of each of the copolymers a ratio was taken of the intensity of the central band of set 1 (312 nm) to that of set 2 (367 nm) and a similar ratio of set 2 (367 nm) to set 3 (412 nm). The ratios obtained from the ultraviolet spectra were in good agreement with the sequence ratios calculated from the copolymerization parameters and thus supports the assignment of each band set to a particular polyene sequence. All of the results are completely in accord with 1,4-addition polymerization of 1-chloro-1,3-butadiene to give structural units 2 which then undergo 1,4-conjugate elimination of HCl to give copolymers having sequences of conjugated unsaturated structures 3.

One of the simplest members of a class of 1-halogenated butadiene monomers is 1-chloro-1,3-butadiene (1). Three paths are available for the polymerization of 1-chloro-1,3-butadiene; 1,4 addition, 1,2 addition, and 3,4 addition to give structures 2, 3, and 4, respectively (Scheme I). Both the 1,4- and the 1,2-addition products 2 and 3 are capable of undergoing elimination of hydrogen chloride to give the conjugated polyene type structures 5 and 6.

Scheme I



We have shown previously that certain similar compounds, the halogenated protoanemonins 7, 8, and 9, readily copolymerize with methyl methacrylate and styrene to give copolymers that indeed evolve hydrogen chloride under mild conditions.[2-5] In the case of 5,5-dichloroprotoanemonin (7) ultraviolet absorption at 367 nm was suggested as originating from a conjugated system containing six double bonds, a feature which could only have arisen from diads of the dichloroprotoanemonin monomer.[4] This interpretation led to the idea that perhaps ultraviolet spectroscopy could be used effectively to study the sequence distribution of copolymers derived from 1-halogenated butadiene monomers. Elimination of HX from such copolymers would provide unsaturated structures with the sequence length being related to the number of conjugated double bonds in the sequence. Each different sequence should then give rise to its own characteristic ultraviolet adsorption spectrum.



protoanemonin

7, 5,5-dichloro-

8, 5,5-dibromo-

9, 3,5-dibromo-

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(1) Presented in part at the IUPAC, International Symposium on Macromolecules, Helsinki, Finland, July 2-7, 1972, Preprint Vol. 1, p 291.

(2) A. Winston and G. T. C. Li, *J. Polym. Sci., Part A-1*, 5, 127 (1967).

(3) A. Winston and D. A. Chapman, *J. Polym. Sci., Part C*, 22, 65 (1968).

(4) A. Winston, D. A. Chapman, and G. T. C. Li, *Amer. Chem. Soc., Div. Polym. Prepr.*, 9, 41 (1968).

(5) A. Winston, M. Quinn, R. Kemper, N. DeMercurio, *Amer. Chem. Soc., Div. Coatings Plastics Chem. Pap.*, 29 (No. 2), 367 (1969).

Table I
Intrinsic Viscosities of Styrene (M_1): 1-Chloro-1,3-butadiene (M_2) Copolymers in Benzene at 36°

f_1	Conversion (%)	$[\eta]$
1.00	50	0.59
0.94	52	0.17
0.89	28	0.12
0.80	23	0.086
0.73	8	0.073

Initial work in this laboratory showed that 1-chloro-1,3-butadiene readily copolymerized with styrene through initiation by gamma radiation from cobalt-60. The copolymers possessed few features above 280 nm in the ultraviolet region. But after being subjected to mild heating or weak bases, a remarkable series of intense, well resolved bands appeared extending up to 500 nm. On the basis of such spectra it is clear that loss of HCl generated a variety of conjugated sequences.

In this paper the course of polymerization (1,4, 1,2, or 3,4 addition) will be established, the ultraviolet absorption bands arising on elimination of HCl will be assigned to particular sequence lengths, and the relative intensities of the bands will be correlated with the statistical sequence distribution as calculated from the reactivity ratios.

Experimental Section

Materials and Equipment. The monomer, 1-chloro-1,3-butadiene, was prepared by Aldrich Chemical Co. by the dehydrohalogenation of *trans*-1,4-dichloro-2-butene according to a procedure modeled after that of Heasley and Lais.[6] The monomer, reported to be a mixture of 85% cis and 15% trans isomers,[6] was checked for purity by Aldrich prior to shipment. Styrene was freshly distilled under reduced pressure. *N,N*-Dimethylformamide (Matheson, Colemann & Bell) was used as received. Polymerization was initiated by γ rays from cobalt-60 contained in 12 ft of water at a dose rate about 0.2 Mrad/hr. Elemental analyses were by Chemalytics, Tempe, Ariz., and Galbraith Laboratories, Inc., Knoxville, Tenn. Ultraviolet spectra were recorded on the Bausch and Lomb Spectronics 505. Viscosities were determined using a Cannon Ubbelohde dilution viscometer. The thermogravimetric balance was manufactured by American Instrument Co. Calculations were made using the IBM 360/75 digital computer.

Copolymerization. The appropriate weight ratios of styrene (M_1) and 1-chloro-1,3-butadiene (M_2) were sealed in heavy wall glass tubes under 1-2-mm pressure of nitrogen. The tubes were placed in copper cylinders and lowered into the cobalt-60 γ ray source at ambient temperatures (about 26°) for varying periods of time ranging from 20 to 180 hr. In general, the greater the amount of 1-chloro-1,3-butadiene content in the feed, the longer the polymerization time required. The containers were opened and the copolymers were precipitated by dilution with methanol. The polymers were reprecipitated several times from benzene-methanol, dried under nitrogen at room temperature for 24 hr, and then submitted for C, H, and Cl analyses.

Results

Characterization of Copolymers. The copolymers of low 1-chloro-1,3-butadiene content are colorless solids, while those containing greater than 50% are pale yellow solids and somewhat unstable since they darken and become heterogeneous after standing in air for a few days. The copolymers are completely soluble in chloroform, acetone, benzene, carbon disulfide, and *N,N*-dimethylformamide and are insoluble in methanol and water.

The ultraviolet spectra of the copolymers showed little absorption above 280 nm. However, on standing for several weeks the bands characteristic of the polymers after HCl elimination had appeared.

Table II
Copolymerization Data for Styrene (M_1): 1-Chloro-1,3-butadiene (M_2)

f_1	Conversion (%)	Anal. C (%)	Anal. Cl (%)	F_1, Calcd from C (%)	F_1, Calcd from Cl (%)	F_1[a] (Av)
0.947	2.5	85.46	6.51	0.820	0.838	0.829
0.892	4.5	81.80	10.88	0.724	0.729	0.726
0.861	6.3	80.11	12.25	0.680	0.695	0.688
0.829	8.9	78.57	14.15	0.639	0.647	0.643
0.734	8.1	74.68	18.01	0.537	0.551	0.544
0.698	7.6	72.55	18.92	0.481	0.528	0.505
0.649	9.6	71.34	20.14	0.449	0.498	0.474
0.602	11.4	70.65	21.17	0.431	0.472	0.452
0.551	9.0	68.93	23.48	0.386	0.415	0.401
0.490	8.6	67.86	25.05	0.358	0.375	0.367
0.448[b]	11.1	67.85	25.39	0.357	0.367	0.362
0.324[b]	8.0	64.95	27.92	0.281	0.304	0.293
0.247[b]	12.4	61.00	30.65	0.178	0.236	0.207
0.221[b]	11.0	61.03	31.23	0.178	0.221	0.200
0.153[b]	10.1	58.69	34.79	0.117	0.133	0.125

[a] Average of values from % C and % Cl. [b] Per cent C and Cl have been corrected for the presence of oxygen.

Table III
Reactivity Ratios for the Styrene (M_1): 1-Chloro-1,3-butadiene (M_2) System

Method		r_1	r_2
Finemann-Ross (r_1 = slope)		0.23	0.98
Finemann-Ross (r_2 = slope)[a]		0.29	1.06
	Av	0.26	1.02
Mayo-Lewis		0.22 ± 0.01	1.07 ± 0.10
Curve fitting		0.23	0.98
	Av	0.23 ± 0.02	1.02 ± 0.10

[a] These data were obtained by switching the assignments of M_1 and M_2.

The intrinsic viscosities of the copolymers are reported in Table I and compared with pure polystyrene prepared under the same conditions as the copolymers.

Reactivity Ratios. The composition of each copolymer was calculated both from the per cent carbon and the per cent chlorine. There was generally satisfactory agreement between the two values and the average value was used for F_1 in the subsequent calculations (Table II). In the last five cases of Table II the C, H, and Cl analysis failed to sum to 100%. Elemental analysis for oxygen content indicated that these copolymers contained oxygen, undoubtedly a result of air oxidation during the isolation procedures. In these cases the analytical results were corrected to take into account the presence of oxygen.

Reactivity ratios were calculated by the Finemann-Ross, Mayo-Lewis, and curve-fitting methods. The computer program of McCaffrey[7] was used to generate r_1,r_2 values for the least-squares fit of the Fineman-Ross plot. Since the r_1,r_2 values are often significantly different depending upon the assignment of M_1 and M_2, the program was run both ways. The results agreed fairly closely and both sets are reported in Table III. The computer program also generates the lines required in the Mayo-Lewis method. This data was then used to generate the Mayo-Lewis plot by means of the Calcomp plotter. The area of maximum intersections was determined and the corresponding r_1,r_2 values are reported in Table III together with an estimation of the probable error.

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(6) V. L. Heasley and B. R. Lais, *J. Org. Chem.*, 33, 2571 (1968).

(7) E. M. McCaffery, "Laboratory Preparation for Macromolecular Chemistry," McGraw-Hill, Inc., New York, N. Y., 1970, pp 362-364.

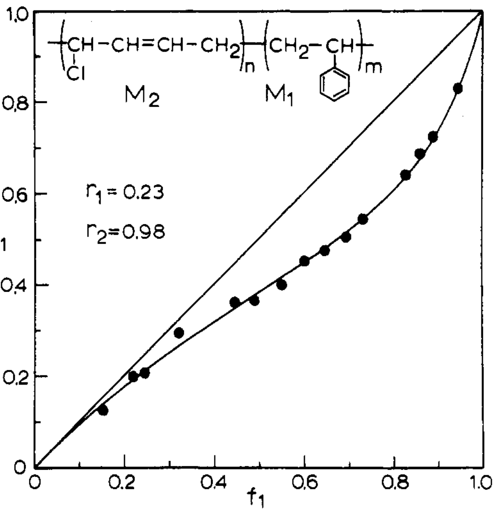

Figure 1. Feed-copolymer composition curve for styrene (M_1):1-chloro-1,3-butadiene (M_2).

A computer program was written to select a pair of r_1, r_2 values which would provide a nonlinear least-squares fit of the feed-copolymer composition curve to the experimental data (Figure 1). The reactivity ratios were in good agreement with those obtained by the other methods and are given in Table III.

Elimination of Hydrogen Chloride. *Direct Heating.* A sample of one of the copolymers was subjected to thermogravimetric analysis and was observed to undergo a weight loss of about 5% at 100° accompanied by a change of color. The ultraviolet spectrum of the copolymer revealed the same series of absorption bands that arise on treatment with base. On continued increase in temperature, a second large weight loss occurred between 350 and 400°, which is characteristic of pure polystyrene.

Heating in Triethylamine-Dimethylformamide. Each copolymer was dissolved in dimethylformamide (1 mg/ml) and 1 mg of triethylamine/10 mg of copolymer was added. The solutions were heated at 160–180° under nitrogen for from 1 to 3 days. Over this period the colors of the solutions changed from light or dark yellow to dark red. Samples were taken periodically, were diluted, and subjected to ultraviolet analysis. At first the intensities of the absorption bands increased on continued heating. However, eventually a maximum would be reached, after which the intensities would decline somewhat. The results given in the subsequent discussions were taken from spectra recorded at or near this maximum. The heating period necessary to achieve the maximum depends upon the copolymer composition; the higher the 1-chloro-1,3-butadiene content, the shorter the time required.

Several samples run at concentrations of 10–20 mg/ml were heated according to the above procedure, and were precipitated from the dimethylformamide solution by dilution with methanol. Isolation and purification of the samples was extremely difficult due to emulsion formation. It took some time before the polymer could be isolated, and after isolation, the polymer was no longer soluble in benzene or dimethylformamide. Thus it became impossible to perform further purification or to record the ultraviolet spectra. The dark-colored dimethylformamide solutions became lighter upon exposure to air over a period of several days. The insolubility and the color change are evidence that the unsaturated copolymer is readily oxidized by air. One sample, which before elimination had contained 4.07% Cl, was successfully purified and was found to contain only 0.1% chlorine, thus indicating that elimination was essentially complete.

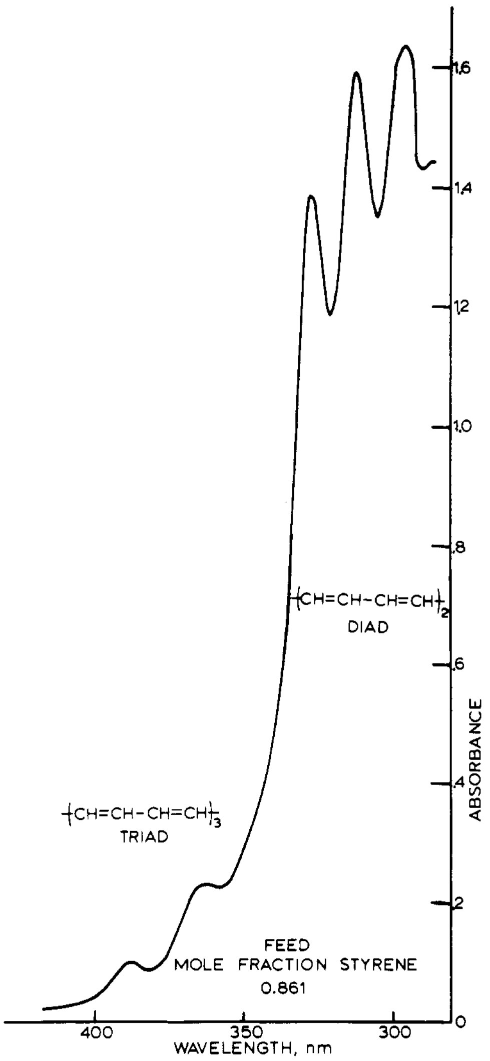

Figure 2. Ultraviolet spectrum of copolymer from 0.861 feed after HCl elimination.

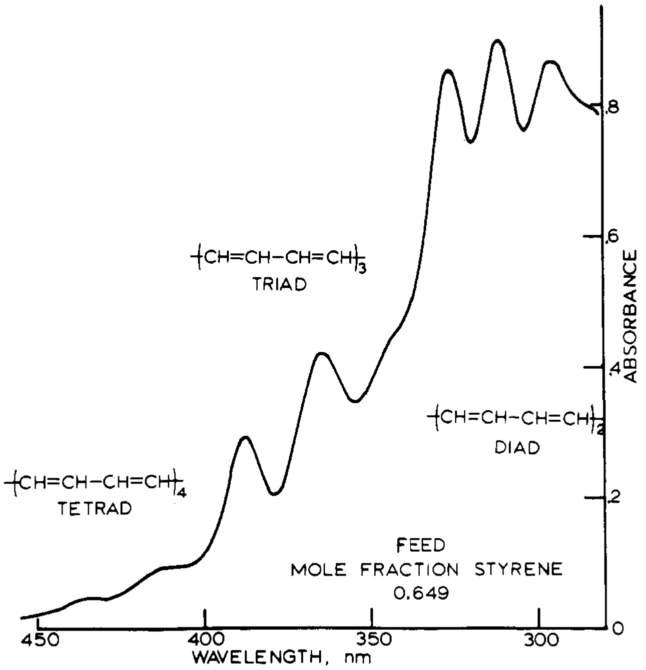

Figure 3. Ultraviolet spectrum of copolymer from 0.649 feed after HCl elimination.

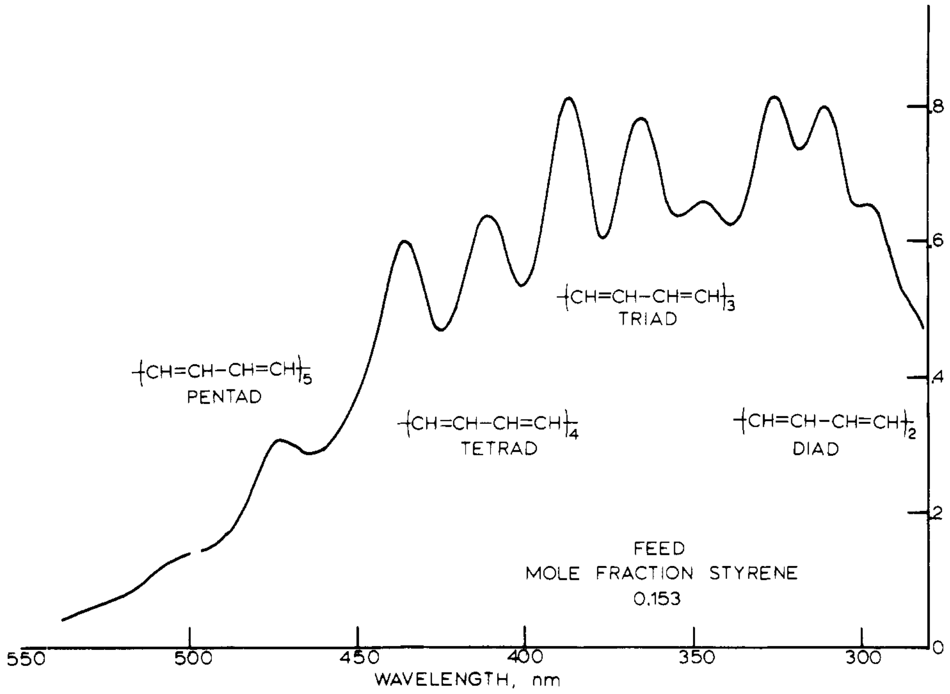

Figure 4. Ultraviolet spectrum of copolymer from 0.153 feed after HCl elimination.

Ultraviolet Spectra. The polymer before being subjected to hydrogen chloride elimination possessed few features above 280 nm. However, weak peaks at 282 and 291 nm were commonly observed, although sometimes the 291-nm band was missing. On elimination of hydrogen chloride, distinct bands appear at 298, 312, 327, 347, 367, 388, 412, 437, 473, and 510 nm.

Sample spectra are shown in Figures 2-4. The specific absorbancies (1% solution) for the copolymers are presented in Table IV.

Table IV
Ultraviolet Data of Copolymers after HCl Elimination

	Specific Absorbance[a] at λ (nm)								
f_1	298	312	327	347	367	388	412	437	473
0.947	46	46	26		5.8	2.8			
0.892	40	47	41		6.3	3.5			
0.861	64	63	55		9.1	3.9			
0.829		74	66		13	5.1			
0.734	82	71	62		19	7.7			
0.698	110	107	101		44	30	9.3	4.1	
0.649	102	106	101		50	35	11	5.3	
0.602	107	97	96		50	32	13	5.9	
0.551	151	154	150		77	53	20	7.9	
0.490	153	151	144		78	71	42	30	
0.448	151	190	192		138	139	80	77	34
0.324	155	193	195		165	170	97	91	54
0.247	166	198	202	142	183	187	104	100	67
0.221	135	168	169	100	103	102	85	73	40
0.153	149	186	191	133	165	162	98	90	55

[a] 1% solution in dimethylformamide.

Discussion

The monomer, 1-chloro-1,3-butadiene, readily copolymerizes with styrene on initiation with gamma rays from a cobalt-60 source. Although other methods of initiation can be used, cobalt-60 was chosen, since under these mild conditions elimination of HCl did not occur to any great extent during the polymerization. Thus the copolymer compositions could be determined from chlorine and carbon analyses.

The intrinsic viscosities of the copolymers decrease with increasing 1-chloro-1,3-butadiene content. This may indicate a lowering of the molecular weight possibly by increased termination rates through disproportionation.

On heating to 100° or through treatment with weak base, such as triethylamine in dimethylformamide, the copolymers rapidly lose hydrogen chloride. The appearance of many intense bands in the ultraviolet spectra reveal that the copolymers now contain a variety of conjugated olefinic structural units.

Concerning the three possible modes of addition (Scheme I), the ease by which the copolymers evolve hydrogen chloride indicates that 3,4 addition is relatively unimportant, as structure 4 would be particularly resistant toward elimination..

On the basis of the reactivity ratios, 1,2 addition can also be shown to be an unlikely path. In 1,2 addition, 1-chloro-1,3-butadiene would be reacting as a 1,2-disubstituted ethylene. The r_2 values for the copolymerization of styrene (M_1) with some 1,2-disubstituted ethylenes (M_2) such as cinnamonitrile, crotononitrile, *cis*-dichloroethylene, maleic anhydride, 1-chloropropene (with vinyl chloride), and methyl cinnamate are much less than one and in most cases approach zero.[8] Also, with few exceptions, the r_1 values approach one or are greater than one. These data indicate that, in general, 1,2-disubstituted ethylene monomers have low intrinsic reactivity in copolymerization. However, in the case of 1-chloro-1,3-butadiene the reactivity ratios (Table III) clearly reveal that this monomer possesses a fairly high reactivity, much higher, in fact, than is normally characteristic of a monomer reacting as a 1,2-disubstituted ethylene. Also, butadiene,[9] chloroprene,[10] and isoprene,[11] are known to react largely by 1,4-addition, and according to their reactivity ratios,[8] pos-

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(8) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook," Interscience Publishers, New York, N. Y., 1966.
(9) R. R. Hampton, *Anal. Chem.*, 21, 923 (1949).
(10) J. T. Maynard and W. E. Mochel, *J. Polym. Sci.*, 13, 251 (1954).
(11) W. S. Richardson, and A. Sacher, *J. Polym. Sci.*, 10, 353 (1953).

Table V
Distribution of 1-Chloro-1,3-butadiene (M_2) in Copolymer

	% M_2 Sequences Containing *n* Units				Calcd Sequence Ratio[a]	Obsd Ratio of Sp Absorbance	
f_1	$n = 1$	$n = 2$	$n = 3$	$n = 4$		312:367 nm	367:412 nm
0.947	94.6	5.01	0.28	0.01	18.9	7.9	
0.892	89.0	9.78	1.07	0.12	9.10	7.4	
0.861	85.9	12.14	1.72	0.24	7.07	6.9	
0.829	82.6	14.36	2.50	0.43	5.75	5.7	
0.734	73.0	19.70	5.32	1.44	3.71	3.7	
0.698	69.4	21.24	6.50	1.99	3.26	2.4	4.7
0.649	64.4	22.91	8.15	2.90	2.81	2.1	4.5
0.602	59.7	24.05	9.69	3.90	2.48	1.9	3.8
0.551	54.6	24.79	11.25	5.11	2.20	2.0	3.9
0.490	48.5	24.98	12.86	6.62	1.94	1.9	1.9
0.448	44.3	24.68	13.74	7.65	1.79	1.4	1.7
0.324	32.0	21.75	14.79	10.07	1.46	1.2	1.7
0.247	24.3	18.41	13.93	10.54	1.32	1.1	1.8
0.221	21.8	17.03	13.32	10.42	1.28	1.6	1.2
0.153	15.0	12.78	10.85	9.22	1.18	1.1	1.7

[a] Calculated sequence ratio is the ratio of M_2 sequences containing *n* units to those containing $n + 1$ units.

sess high reactivity, which is completely in accordance with the observed high reactivity of 1-chloro-1,3-butadiene. On the basis of these comparisons, we conclude that little or no 1,2 addition of this monomer occurs.

The infrared spectra of the copolymers support this interpretation. Bands characteristic of the vinyl group[9] do not appear at 990 and 911 cm^{-1}. A strong band appears at 960 cm^{-1}, which is consistent with the presence of a trans-disubstituted olefin.[9] Bands for the corresponding *cis*-olefin generally could not be observed due to overlapping with the 690- and 750-cm^{-1} bands of polystyrene. However distortion of these bands is apparent, and in one case a clear peak at 720 cm^{-1} was resolved and may be due to cis 1,4-addition structures. On elimination of HCl the 960-cm^{-1} peak vanishes and a broad band appears at 1650 cm^{-1} characteristic of a conjugated diene.

As is often characteristic of polymers, the nmr spectra are generally lacking in detail. A broad band appears at τ 6.4–6.8, which is in the region of 1,2-disubstituted ethylenes. Since no resonance lines at τ 5.0–5.6 were visible, pendant vinyl groups are not an important structural feature. On elimination of HCl the τ 6.4–6.8 band is essentially eliminated.

Thus the spectroscopic evidence supports the idea that polymerization of 1-chloro-1,3-butadiene proceeds essentially by 1,4 addition to give structure 2 (Scheme I) which on elimination of HCl gives the conjugated unsaturated copolymer 5 in which the unsaturation is located within the main chain.

Figures 2–4 illustrate the appearance of the ultraviolet spectra of several copolymers after HCl elimination and over a wide range of copolymer compositions. Studies of the ultraviolet spectra of model polyenes containing from 3 to 12 conjugated double bonds have shown that the principal feature of any polyene is a set of three bands of about equal intensity and separated by from 15 to 25 nm.[12,13] With this in mind the absorption bands of the copolymers can be classified into four sets, where the bands within each set retain the same relative intensities regardless of the composition of the copolymer. The three bands of set 1 (298, 312, 327 nm) are clearly resolved. The three bands of set 2 (347, 367, 388 nm) can be distinguished, but the lower wavelength (347 nm) band often exhibits considerable overlap with the 327-nm band of set 1, although in several cases this band was completely resolved. Only two bands (412, 437 nm) of set 3 can be seen, but presumably there is another lying under the 388 nm band of set 2. Only one band of set 4 (473 nm) appears, but the other two must overlap with the 437-nm band of set 3. A very weak band at 510 nm may be a part of a fifth set (Figure 4).

The positions of these sets of bands is consistent with the following assignments to particular sequences. The three bands of set 1 are in the correct location for four conjugated double bonds representing a diad derived from 1-chloro-1,3-butadiene monomer residues. Similarly, the absorption bands of set 2 correspond to six double bonds (triad); set 3, to eight double bonds (tetrad); and set 4, to ten double bonds (pentad). As the composition of the copolymer changes, the relative intensities of the sets themselves exhibit significant changes in exactly the manner expected from the changing distribution of conjugated olefinic sequences. The fact that the bands within a set retain their relative intensities, regardless of the copolymer composition, indicates that each set arises from one particular structural unit. Also, the specific absorbancies of all bands increase consistently with increasing polyene content.

The sequence distribution of $-(CH{=}CHCH{=}CH)_n-$ structures in the copolymers were calculated on the computer from the values of r_1, r_2, and f_1 for sequence lengths of n = 1–4. These data are given in Table V together with the sequence ratio, defined as $\%n$ sequence/$\%(n + 1)$ sequence. The ratios of the specific absorbance of the central ultraviolet bands of set 1 (312 nm) to set 2 (367 nm) and of set 2 (367 nm) to set 3 (412 nm) for each copolymer was determined and these data are compared in Table V with the sequence ratios calculated from the copolymerization parameters. The central band of each set was used in this comparison because this one would experience less overlap with bands from neighboring sets.

The specific absorbance ratios of the 312-nm band to the 367-nm band of the various copolymers are in excellent agreement with the sequence ratios calculated from the copolymerization parameters with one exception. In the case of $f_1 = 0.947$ the discrepancy may be attributed to error introduced from band overlap due to the great difference in intensity between the 312- and the 367-nm

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(12) F. Bohlmann and J. H. Mannhardt, *Chem. Ber.*, 89, 1307 (1956).
(13) P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 3037 (1955).

bands. The ratios of the 367- to the 412-nm band also agrees reasonably well with the calculated sequence ratios. However, since the bands become closer together as we go to higher wavelengths, overlapping becomes more severe and the intensity measurements, particularly of the 412-nm band, are less precise.

The agreement of the observed ratios with the calculated ratios supports the original assignments of the sets to diads, triads, tetrads, and pentads derived from conjugated diene sequences, and is consistent with a structure arising from 1,4 addition of 1-chloro-1,3-butadiene. These results confirm once again the validity of the theory underlying sequence distribution calculations from copolymerization data. There are few cases which permit such a direct analysis of sequence distribution in copolymerization.

Structural Studies of Isotactic Poly(*tert*-butylethylene oxide)

Hideko Sakakihara, Yasuhiro Takahashi, Hiroyuki Tadokoro,* Nobuki Oguni, and Hisaya Tani

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, 560 Japan. *Received September 22, 1972*

ABSTRACT: The crystal structure (one of two crystal modifications) of the racemic sample of isotactic poly(*tert*-butylethylene oxide) was investigated by utilizing the X-ray diffraction method and conformational energy calculation. This polymer has a true asymmetric carbon atom in each monomeric unit, giving two types of optical isomers; rectus (*R*) and sinister (*S*). The unit cell is tetragonal, $P\bar{4}n2\text{-}D_{2d}^{8}$, with a = 15.42 Å and c (fiber axis) = 24.65 Å. The molecular chain has a helical structure and nine monomeric units turn four times along the helix in the fiber identity period. Four molecules of the (9/4) helix pass through the unit cell and two pairs of optical antipodes exist in definite positions in the unit cell. Consequently the unit cell is optically inactive. The result of the analysis also suggests the formation of two types of isotactic polymer chains from the mixture of *R* and *S* monomers in polymerization with diethylzinc–water as catalyst.

Poly(*tert*-butylethylene oxide) has a true asymmetric carbon atom in each chemical monomeric unit, $O\text{-}CH_2\text{-}C(\text{-}CMe_3)H$, and so there are two kinds of optical isomers in the case of the isotactic polymer chain. These planar zigzag models and the corresponding Fischer projections are illustrated in Figure 1. According to the nomenclature proposed by Cahn, Ingold, and Prelog,[1] the absolute configurations of these two optical isomrs can be indicated by rectus (*R*) and sinister (*S*). In the case of the racemic sample, both the optical isomers of the isotactic polymer chains must coexist. Therefore it is an interesting problem to determine the arrangement of two kinds of optical antipodes in the crystalline state. From this point of view, the structural studies of isotactic poly(*tert*-butylethylene oxide) are closely related to those of isotactic poly(propylene oxide)[2-5] and isotactic poly(propylene sulfide).[6]

Since crystalline poly(*tert*-butylethylene oxide) was synthesized,[7-11] the crystal structure has not yet been reported by any authors. In the present work, the crystal structure of the racemic sample was investigated by using mainly X-ray diffraction. It should be noted that the two most reasonable molecular models could be selected through the calculations of the intramolecular interaction energies according to the procedure as already described in the previous papers.[12-14] There are only a few examples[15-17] to which the conformational analysis has been applied for this purpose.

Experimental Section

Samples. The substance used in this study was polymerized from racemic *tert*-butylethylene oxide using diethylzinc–water (1:07) as catalyst, and the benzene-insoluble part of the raw polymer was used. The melting temperature measured by using a polarizing microscope was 136°. In this study, two kinds of crystal modifications were formed depending upon the conditions of crystallization. They were designated modifications I and II. A good crystalline and well-oriented sample of modification I was prepared by stretching a strip of an amorphous sample (prepared by quenching from melt) at about 120°, and annealing at about 110° under tension using a metal holder. On the other hand, a uniaxially oriented specimen of modification II was prepared by stretching a strip of a melt-quenched sample at a temperature a few degrees below the melting point, followed soon after by heat treatment at 130° under tension.

X-Ray Measurement. Throughout the present study, the X-ray photographs were taken by using nickel-filtered Cu Kα radiation. A cylindrical camera (diameter 10.0 cm) and a Weissenberg camera (diameter 9.0 cm) were used. The camera radii were corrected with the spacings of the reflections of aluminum powder. Reflection intensities obtained by the multiple film method were estimated visually by use of the standard intensity scale.

The fiber photographs of modifications I and II of poly(*tert*-butylethylene oxide) are given in Figures 2a,b, respectively. Figure 3 shows the Weissenberg photograph with its schematic representation which was taken by setting the uniaxially oriented specimen with the fiber axis perpendicular to the camera axis,

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