rate of molecule formation is really the same comparison which was made in Table II. While the initial rates of polymer particle formation are consistently lower than the rates of molecule formation, not much significance can be attached to this because of the larger error and uncertainty involved in calculating the initial rate of particle formation. Of the three methods for determining the rate of free radical formation by the initiation reaction, the rate of molecule formation is the most reliable.

Summary

The rate of persulfate combination from radioactivity measurements, the initial rate of polymer particle formation from polymer particle size measurements, and the rate of molecule formation from molecular weight measurements have been obtained for styrene emulsion polymerization, and all three quantities agree within an order of magnitude. This indicates that all three are determined principally by the rate of formation of free radicals.

The rate of free radical formation does not appear to depend on the interfacial area between organic and aqueous phases.

PASSAIC, N. J. RECEIVED APRIL 27, 1949

[CONTRIBUTION NO. 262 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

The Structure of Neoprene. IV. Infrared Spectra and Spectral Changes with Crystallization[1]

BY W. E. MOCHEL AND M. B. HALL

Infrared spectroscopy has been valuable in elucidation of some structural features of high polymers and was therefore applied to the current examination of neoprene (polychloroprene). The infrared spectrum of neoprene has been reported previously[2] and the statement has been made that there are differences between polychloroprenes made under different conditions of polymerization.[3] However, no description of the differences has appeared. In the present study, examination of Neoprenes Type GN and Type CG and analysis of the dichroic effects in their spectra together with comparison with the infrared absorption of polybromoprene have yielded a more complete and reliable interpretation of the spectrum of neoprene than was previously available. These particular neoprenes were selected for study because they are illustrative of the effect of polymerization temperature on the rate of crystallization,[4] *i. e.*, Neoprene Type CG, made at 10°, crystallizes in a few hours at room temperature while Neoprene Type GN, made at 40° in essentially the same emulsion system, requires many days for crystallization to a comparable extent. The crystallization of neoprenes in general has been well established[5] by X-ray diffraction, dilatometry and other methods but the structural differences responsible for observed differences in crystallization rates have not been clearly demonstrated.

Experimental

Materials.—For many of the experiments commercial samples of Neoprene Type CG and Neoprene Type GN were used. To remove undesirable polymerization adjuvants from such samples, they were extracted with acetone in A.S.T.M. extractors or were dissolved in benzene and completely precipitated with methanol. Laboratory samples were also prepared using the emulsion system previously described.[4] The polymers were isolated from the alkaline latices by coagulation with large volumes of alcohol, since it was found that this procedure gave products practically free from sodium rosinate, rosin and other polymerization residues. The polymers were dried *in vacuo* at room temperature and kept under nitrogen.

To prepare films the dry polymers were dissolved in benzene to form solutions of known concentration which were used to cast films inside glass rings on a mercury surface. After the film was dry the ring could be lifted and the attached film examined directly or transferred to another specimen holder. Films were also prepared directly from the latices by filtration on porous battery cups.[6] Films 20–35 microns in thickness were generally used for infrared studies.

Instruments.—Two different instruments were used to obtain the data presented here. For most of the work in the wave length range 2–14 microns there was used a prism instrument after

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(1) Part III, Mochel and Nichols, THIS JOURNAL, **71**, 3435 (1949).

(2) Sears, *J. Appl. Phys.*, **12**, 35 (1941); Barnes, Williams, Davis and Giesecke, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 9 (1944); Dinsmore and Smith, *Anal. Chem.*, **20**, 11 (1948).

(3) Thompson and Torkington, *Trans. Faraday Soc.*, **41**, 255 (1945).

(4) Walker and Mochel, Proc. Inter. Rubber Tech. Conf., London, 1948, Preprint No. 11.

(5) (a) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931); (b) Sebrell and Dinsmore, *India Rubber World*, **103**, No. 6, 37 (1941); (c) Bunn, *Proc. Roy. Soc.* (*London*), **A180**, 82 (1942); (d) Clews, *ibid.*, **A180**, 100 (1942); (e) Wood, "Advances in Colloid Science," Vol. 2, edited by Mark and Whitby, Interscience Publishers, Inc., New York, N. Y., 1946, p. 79.

(6) Dales, Abernathy and Walsh, "Neoprene Latex Type 571," No. 43-2, du Pont Rubber Chemicals Division, February, 1943; Flint, "Chemistry and Technology of Rubber Latex," D. Van Nostrand Company, Inc., New York, N. Y., 1938, p. 688.

the design of Wright,[7] employing a 60° rock salt prism with a six-inch base. The 2–4-micron range was examined in the same instrument at a resolution sufficient to show clearly the chlorine isotope split in hydrogen chloride, by replacing the prism with a 7200-lines-per-inch grating. The recording system employed a split beam and the ratio recorder described by Wild.[8]

In most of the work a Nernst filament was used as source for the 15–23-micron region to avoid the sharp minimum at 16.2 microns in the globar emission. The radiation was polarized when desired by reflecting it at the Brewsterian angle from a selenium mirror according to the method of Pfund.[9] Since the beam striking the selenium mirror is converging, all the rays cannot be incident at exactly the Brewsterian angle, and hence complete polarization cannot be achieved.[10] However, this was not an important limitation since complete orientation could not be produced in the polymer samples under study. In general, the absorption bands reported are accurate to 5 wave numbers except in the cases of overlapping bands, where somewhat greater error may be involved.

For some of the work in the range 2-15 microns and for all of the work at longer wave lengths, a Perkin–Elmer spectrometer was used with a rock salt prism for some purposes and a potassium bromide prism for others. The light entering the Perkin–Elmer instrument was polarized when desired by use of the selenium mirror. The reflection from the selenium mirror was arranged to cause reinforcement of the polarization produced by the prism in the spectrometer.

Results and Discussion

Crystallization Effects.—The most striking feature in the spectra of the neoprenes is the existence in crystallized polymer of strong bands which do not appear in the completely amorphous material. Thus Neoprene Type CG, normally crystalline at room temperature, exhibits absorption bands at 578, 781 and 955 wave numbers (cm.$^{-1}$) which do not appear in the spectrum of the non-crystalline Neoprene Type GN (Fig. 1). These bands do not appear in the spectrum of Neoprene Type CG until the polymer crystallizes and they are present in the spectrum of Neoprene Type GN when the polymer is crystallized by stretching to 800–1000% elongation. (A very weak band at 781 cm.$^{-1}$ appeared in the spectra of some aged, unstretched Neoprene Type GN samples.) They can also be intensified in crystalline Neoprene Type CG by stretching the sample and examining it in that condition. Although these bands appear in the spectrum for Neoprene Type GN examined while it is stretched, a stretched and then relaxed sample fails to show the bands. Furthermore, these absorption bands disappear from the spectrum of a sample of Neoprene Type CG heated to 50° to melt the crystallites. These absorption bands therefore definitely appear to be associated with crystallization in neoprene.[11]

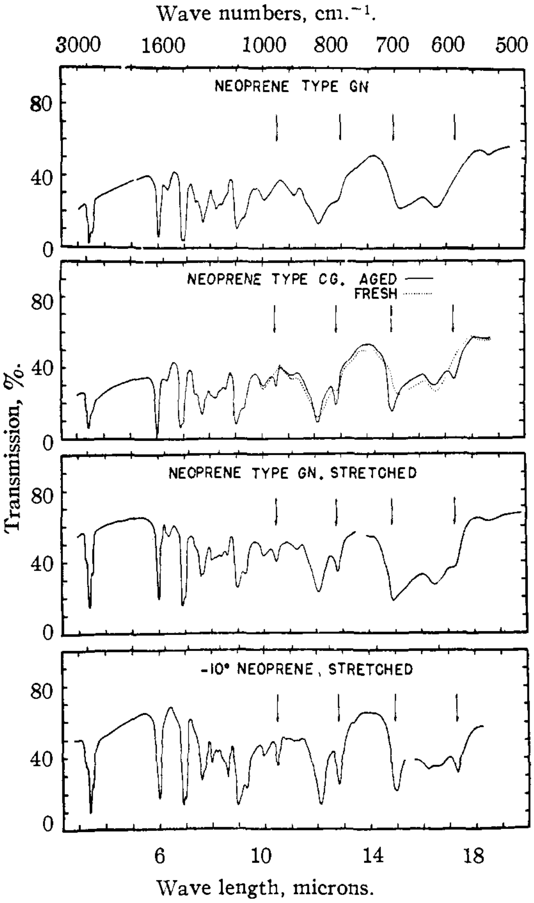

Fig. 1.—Comparison of the infrared spectra of unstretched Neoprene Type GN one day old, unstretched Neoprene Type CG fresh and one day old, stretched Neoprene Type GN and stretched neoprene made at −10°. The arrows indicate absorption bands which are associated with crystallization.

It was also found that a band maximum at 658 cm.$^{-1}$ exhibited by both polymers is greatly enhanced by crystallization and shifted some 10 cm.$^{-1}$ to 667 cm.$^{-1}$. Crystallization causes less pronounced spectral changes in a group of maxima between 1150 and 1250 cm.$^{-1}$ amounting essentially to an increase in intensity of the bands at

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[7] Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).

[8] Wild, *Rev. Sci. Instruments*, **18**, 436 (1947).

[9] Pfund, *Astrophys. J.*, **24**, 19 (1906).

[10] Since the work described here was done, Pfund has designed an improved polarizer which overcomes this difficulty; see Pfund, *J. Optical Soc. Am.*, **37**, 558 (1947).

[11] Differences in the spectra of low molecular weight materials as a result of state of aggregation have been reported: *e. g.*, see Thompson, *Nature*, **158**, 234 (1946), and Richards and Thompson, *Proc. Roy. Soc.*, (*London*), **A195**, 1 (1948). Williams and Taschek, *J. Appl. Phys.*, **8**, 497 (1937), observed in the spectrum of natural rubber stretched radially, the appearance of a relatively intense band at 2084 cm.$^{-1}$ where there is no intense absorption in the unstretched material.

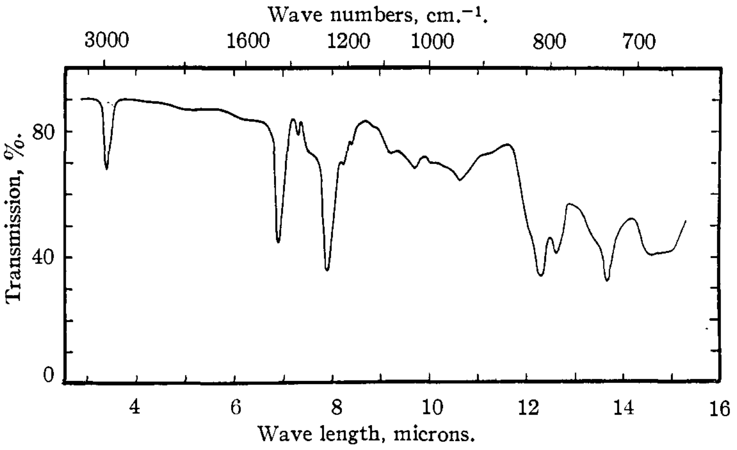

Fig. 2.—Infrared absorption spectra of chlorinated neoprene.

1162 and 1250 cm.$^{-1}$. A weak, perpendicular band which is enhanced by crystallization occurs at about 475 cm.$^{-1}$ in the spectra of crystalline samples. Its presence in other records is doubtful because of the overlapping water vapor rotation lines.

An experimental polychloroprene[12] made at −10° crystallizes in a few seconds, compared to hours for Neoprene Type CG and days for Type GN, but with the exception of somewhat greater intensity in the crystalline-phase bands, it shows no marked spectral differences from Neoprene Type CG.

Except for these crystalline-phase bands there appear to be no significant differences qualitatively among the infrared absorption patterns of the various neoprenes under discussion.[13] Careful examination at high resolution in the 3-micron region, using a grating, revealed no differences in C–H vibrations. There was no evidence for the presence of side vinyl groups from 1,2- or 3,4-addition polymer.[14] Furthermore, chlorinated neoprenes[15] made from both Type GN and Type CG appeared identical in infrared absorption, indicating no difference in structure (Fig. 2). Of course, any geometrical differences in arrangement about the double bonds of the respective neoprenes would be lost on chlorination.

Dichroism.—Examination of stretched Neoprenes Type CG and Type GN with polarized infrared radiation revealed a strong dichroism.[16] The crystalline-phase bands are very prominent for stretched films examined with direction of stretch perpendicular to the vibration plane[17] but are absent or relatively insignificant when the direction of stretch is parallel to the vibration plane (Fig. 3). In addition, several other absorption bands of stretched neoprene are dichroic. For example, it has been shown that the band at 1667 cm.$^{-1}$ in neoprene is similar in dichroism to that of balata, the natural *trans*-polyisoprene. In both polymers this band has maximum intensity when the direction of stretch is perpendicular to the vibration plane. On the other hand, the 1667 cm.$^{-1}$ band of Hevea

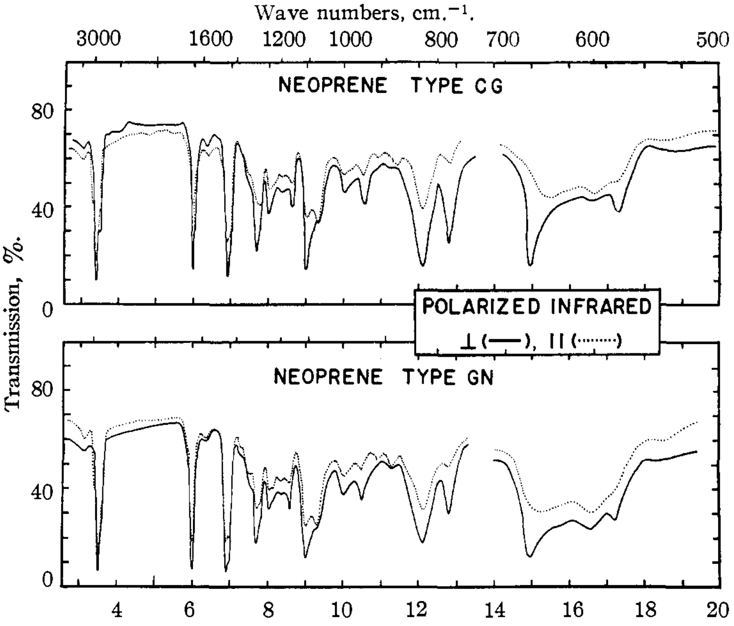

Fig. 3.—Comparison of infrared absorption of stretched Neoprene Type CG and Neoprene Type GN when examined with polarized infrared radiation. Perpendicular (⊥) refers to results obtained when the direction of stretch was perpendicular to the vibration plane.

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[12] The authors are indebted to Dr. R. S. Barrows of the Organic Chemicals Department, Jackson Laboratory, E. I. du Pont de Nemours and Company, for supplying this polymer.

[13] The spectra exhibit slight quantitative differences which have not been completely established as yet.

[14] Unpublished ozonolysis studies confirm the absence of appreciable amounts of side vinyl groups. *Cf.* also Rabjohn, *et al.*, THIS JOURNAL, **69**, 314 (1947).

[15] Carothers, U. S. Patent 2,067,172, Jan. 12, 1937.

[16] There have appeared in the literature several reports of other studies of polymers by means of polarized infrared. See Thompson and Torkington, *Trans. Faraday Soc.*, **41**, 260 (1945); Mann and Thompson, *Nature*, **160**, 17 (1947); Thompson, *J. Chem. Soc.*, 289 (1947); Sutherland and Jones, *Nature*, **160**, 567 (1947); Elliott and Ambrose, *ibid.*, **159**, 641 (1947); Glatt and Ellis, *J. Chem. Phys.*, **15**, 880, 884 (1947); *ibid.*, **16**, 551 (1948); Elliott, Ambrose and Temple, *ibid.*, **16**, 877 (1948).

[17] A band that is stronger when the direction of stretch and the vibration plane are perpendicular than when they are parallel will be referred to as a "perpendicular" band as distinct from a "parallel" band, the intensity of which is a maximum when the vibration plane and direction of stretch are parallel.

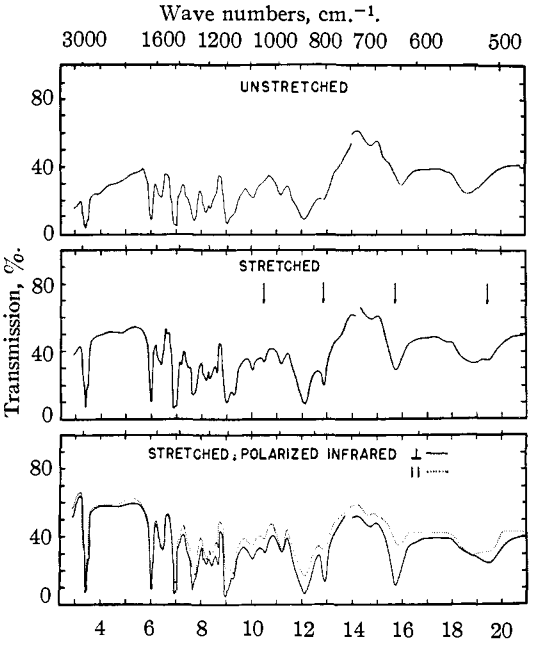

Fig. 4.—Infrared absorption spectra of polybromoprene unstretched, stretched approximately 500% and examined with polarized infrared radiation.

rubber, the *cis*-isomer,[18] has its maximum intensity when the direction of stretch is parallel to the vibration plane of the polarized radiation.[19]

Polybromoprene.—To ascertain which of the bands in the neoprene spectrum result from vibrations involving the C–Cl bonds, samples of polybromoprene[20] were prepared at 40° and their infrared spectra studied using both polarized and non-polarized radiation (Fig. 4). The spectra obtained were very similar, even with respect to dichroism and effects of crystallization, and they demonstrated that the vibrations appreciably involving the C–Cl bonds all lie at longer wave lengths than 15 microns (667 cm.$^{-1}$). The band at 826 cm.$^{-1}$ (12.1 microns) in all polychloroprene spectra and the band that appears at 781 cm.$^{-1}$ when the sample is stretched or when crystallization occurs on aging, occur at 824 and 776 cm.$^{-1}$, respectively, in the polybromoprene spectrum.

Poly-2,3-dichloro-1,3-butadiene.—Another reference compound examined was poly-2,3-dichloro-1,3-butadiene,[21] which was informative in indicating that the band at 1078 cm.$^{-1}$ in the neoprene spectrum involves a bending of the olefinic C–H bond in the plane parallel to the chains. Such a vibration is expected to give rise to a band in the neighborhood of 1100 cm.$^{-1}$. The band at 1078 cm.$^{-1}$ in the neoprene spectrum, rather than the one at 1112 cm.$^{-1}$, is probably the expected one since the only band near this position in the spectrum of polydichlorobutadiene, which has no olefinic C–H, is a perpendicular band at 1095 cm.$^{-1}$ resembling the 1112 cm.$^{-1}$ band of neoprene (Fig. 5). The 1078 cm.$^{-1}$ band, on the other hand, shows little or no dichroism. The various other C–H bending and stretching and double bond stretching bands occur at the expected positions.

A hysteresis in the relation between polarized infrared absorption and stretching was indicated in the case of Neoprene Type GN, suggesting a slow change in ordering or orientation following stretching. The dichroism of the bands at 578, 667, 781 and 955 cm.$^{-1}$ increased slowly over a period of several days following stretching.

Molecular weight was eliminated as an important factor in the changes of infrared absorption observed since no significant differences were found in the spectra of fractions of Neoprene Type CG ranging from 23,000 to 210,000 and fractions of Neoprene Type GN ranging from 44,000 to 250,000 in molecular weight. Furthermore, there were no apparent differences between sol and gel samples of the same polymer.

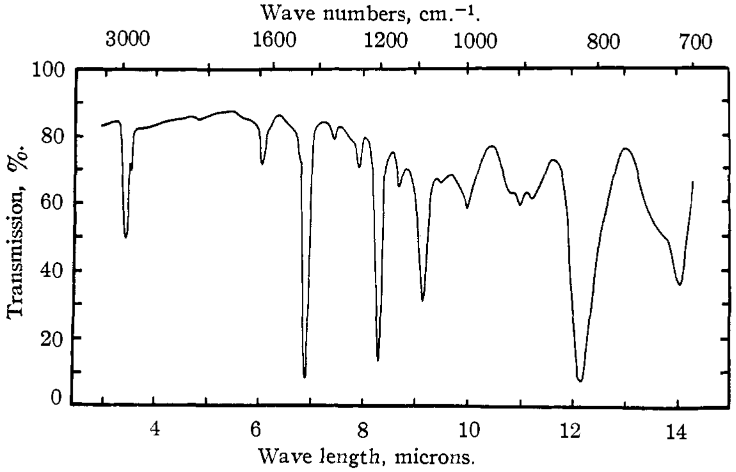

Fig. 5.—Infrared absorption of poly-2,3-dichlorobutadiene examined unstretched.

Interpretation of Results

Table I gives a description of representative neoprene spectra and lists assignments, some of them tentative, of the stronger bands to vibrating groups.

Neglecting small frequency (less than about 5 cm.$^{-1}$) and intensity differences, the only prominent bands present in neoprene, but absent in

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[18] Meyer and Mark, *Ber.*, **61**, 1939 (1928); Fuller, *Ind. Eng. Chem.*, **28**, 907 (1936); Bunn, *Proc. Roy. Soc.* (*London*), **A180**, 40, 67, 82 (1942).

[19] Sutherland and Jones, *Nature*, **160**, 567 (1947).

[20] Carothers, Kirby and Collins, THIS JOURNAL, **55**, 789 (1933).

[21] Berchet and Carothers, *ibid.*, **55**, 2004 (1933).

Table I

Infrared Spectra and Interpretation

Observed bands,[a] in cm.$^{-1}$

Neoprene Type GN		Neoprene Type CG					−10° Neoprene	Polybromoprene			
Non-polarized infrared		Non-polarized infrared			Polarized stretched		Non-polarized stretched	Non-polarized infrared		Polarized stretched	
		Unstretched									
Unstretched	Stretched	Fresh	Aged	Stretched	⊥[c]	∥[c]		Unstretched	Stretched	⊥	∥
	580		578	580	578	584[b]	580		505	505	505[b]
602	602	602	602	602	602	602	602	530	530	530	530
658	667	656	667	667	670	658	670	625	635	638	633
780[b]	780	781[b]	781	781	781	781[b]	781	776[b]	776	776	776[b]
826	826	826	826	826	826	826	826	824	824	824	824
890[b]	890	890	890[b]	890[b]	890[b]	890	890[b]	893	893	893	893
927[b]	927	927	927[b]	927[b]	927	927	927				
	955		955	955	955	955	955		953	953	953
1002	1002	1002	1002	1003	1002	1002	1002	1000	1000	1000	1000
1078	1078	1078	1078	1078	1078	1078	1078	1075	1075	1075	1075
1113	1116	1112	1116	1117	1121	1112	1120	1105	1110	1118	1105
1162	1162	↑	1162	1162	1162	1162	1162	1156	1156	1156	1156
1195	1195		1195	1195	1195	1195	1195	1195	1195	1195	1195
1225	1225		1225	1225	1225	1225	1225	1220	1220	1220	1220
1250	1250		1250	1250	1250	1250	1250	1250	1250	1250	1250
1305	1305		1305	1305	1305	1305	1305	1300	1300	1300	1300
1315	1315		1315	1315	1315	1315	1315	1312	1312	1312	1312
1432	1432	No	1432	1432	1432	1432	1432	1432	1432	1432	1432
1449	1449	data	1449	1449	1449	1449	1449	1439	1439	1439	1439
				1563	1563	1563		1563	1563	1563	1563
1667	1667		1667	1667	1667	1667	1667	1667	1667	1667	1667
2860	2860		2860	2860	2860	2860	2860	2860	2860	2860	2860
2940	2940		2940	2940	2940	2940	2940	2940	2940	2940	2940
3010	3010	↓	3010	3010		3010	3010	3000	3000	3000	3000

[a] Potassium bromide prism used for region 450 to 700 cm.$^{-1}$; rock salt prism used for region 700 to 4000 cm.$^{-1}$. [b] Very weak bands which are sometimes imperceptible. A very weak absorption in some neoprene spectra near 475 cm.$^{-1}$ has been neglected. [c] A perpendicular band (⊥) has maximum absorption when the direction of stretch is perpendicular to the vibration plane. A parallel band (∥) has maximum absorption in parallel position.

polybromoprene, are those at 578 and 667 cm.$^{-1}$ and the broad absorption around 602 cm.$^{-1}$. These bands in neoprene have certain characteristics that serve to identify the corresponding bands in the polybromoprene spectrum. The band that appears at 578 cm.$^{-1}$ at the edge of the broad 602 cm.$^{-1}$ absorption in the spectrum of crystalline neoprene, but not in amorphous neoprene, is a perpendicular-type band. A much weaker band at 505 cm.$^{-1}$, a shoulder only, at the edge of the 530 cm.$^{-1}$ absorption is probably the corresponding band in the polybromoprene spectrum, since it also is a perpendicular band with intensity in the unstretched polymer diminished relative to that in the stretched polymer.

The 658 cm.$^{-1}$ band of non-crystalline neoprene appears with greatly enhanced intensity and with its peak shifted some 10 cm.$^{-1}$ to 667 cm.$^{-1}$ in the crystalline neoprene. It is likewise a perpendicular-type band. The band in the stretched polybromoprene spectrum at 635 cm.$^{-1}$ behaves similarly in each respect and otherwise resembles the 667 cm.$^{-1}$ band of neoprene. It is therefore believed to arise from a vibration of the same form.

The absorption in neoprene with its center at 602 cm.$^{-1}$ and that in polybromoprene with its center at 530 cm.$^{-1}$ probably arise from the same vibrations, since they are both broad absorptions insensitive to crystallization and only very slightly dichroic in stretched samples.

Evidently, then, the vibrations giving rise to bands at 578, 602 and 667 cm.$^{-1}$ in the neoprene spectrum strongly involve the C–Cl bond. Of these, the 578 and 602 cm.$^{-1}$ bands apparently result from vibrations in which the chlorine component is about the same as it would be in a hypothetical diatomic radical C–Cl, since replacement of chlorine by bromine shifts the bands about the amount estimated for a similar sub-

TABLE I (*Continued*)

Remarks	Assignments
Shifted about 70 cm.$^{-1}$ by Cl $\rightarrow$ Br substitution. Appears with crystallization. Strongly perpendicular[c]	Vibrations involving CCl bond strongly. Cl motion about same as in simple CCl structure
Broad (about 50 cm.$^{-1}$). Shifted about 70 cm.$^{-1}$ by Cl $\rightarrow$ Br substitution. Very little dichroism	
Peak frequency decreased about 30 cm.$^{-1}$ by Cl $\rightarrow$ Br substitution. Strongly enhanced by crystallization. Strongly perpendicular	Vibration involving CCl bond. Cl motion less than in simple CCl
Appears with crystallization. Very strongly perpendicular. Frequency lowered about 5 cm.$^{-1}$ by Cl $\rightarrow$ Br substitution	
Shoulder at about 855 cm.$^{-1}$ fades and band narrows with crystallization. Strongly perpendicular	Probably CH_2 deformation vibration
Very weak, parallel band. Stronger, but less parallel in polybromoprene	
Very weak, parallel band	
Appears with crystallization. Strongly perpendicular	Suggest sum frequency: 955 = 781 + 174
	Suggest sum frequency: 1002 = 826 + 176
Apparently little or no dichroism	Olefinic CH parallel bending vibration
Strongly dichroic	
Envelope of four overlapping bands; 1162 and 1250 cm.$^{-1}$ bands strongly perpendicular and enhanced by crystallization, especially stretching	
Other overlapping shoulders at about 1290, 1350 and 1390 cm.$^{-1}$; 1315 cm.$^{-1}$ band strongly perpendicular	
Apparently perpendicular	CH_2 bending vibrations
Perpendicular	
Broad absorption sometimes present	
Perpendicular	Double bond stretching vibration
At least five bands on grating records: at about 2835, 2850, 2920, 2950, and 3020 cm.$^{-1}$ for neoprenes; at about 2825, 2840, 2915, 2945 and 3000 cm.$^{-1}$ for polybromoprene	Saturated CH stretching
	Olefinic CH stretching

stitution in the C–Cl radical. In the case of the 667 cm.$^{-1}$ band the shift is less than that predicted for the C–Cl radical. The band at 826 cm.$^{-1}$, which appears in the spectra of all neoprenes, cannot involve the C–Cl bond appreciably because it occurs within two wave numbers of the same place in the polybromoprene spectrum. The high intensity of this 826 cm.$^{-1}$ band in neoprene and the fact that it is strongly perpendicular suggest that it arises from a vibration consisting essentially of a hydrogen deformation, since it does not arise from a vibration involving the chlorine atom.[22]

The similarities between the bands at 781 cm.$^{-1}$ and 955 cm.$^{-1}$ and between those at 826 cm.$^{-1}$ and 1002 cm.$^{-1}$ suggest that the 955 and 1002 cm.$^{-1}$ bands are sum frequencies involving a vibration of about 175 cm.$^{-1}$ plus the 781 and 826 cm.$^{-1}$ bands, respectively.

The appearance of strong absorption bands as a result of crystallization of the polymer is a phenomenon that apparently has not been recognized previously in high polymers. Evidently it is a factor that must not be neglected in the interpretation of the spectra of polymers. In the spectrum of neoprene the crystalline-phase bands appear to be associated with several different vibrations. The band at 578 cm.$^{-1}$ involves strong motion of the chlorine atom while those at 781 and 955 cm.$^{-1}$ involve very little. All of these bands are of maximum intensity in the oriented polymer when the vibration plane and direction of stretch are perpendicular and are absent or nearly so when the vibration plane and direction of stretch are parallel.

That such bands should appear as a result of crystallization is curious. One might have expected a large decrease—rather than an increase—in the intensity of a strongly dichroic band as a result of simply orienting the sample, as in stretching. For, neglecting background, a perfectly oriented sample would be transparent to one

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(22) A perpendicular band at 735 cm.$^{-1}$ in polythene has been assigned to a hydrogen deformation vibration on the basis of deuterium substitution data; Sheppard and Sutherland, *Nature*, **159**, 739 (1947).

component of radiation of the wave length of a completely perpendicular or parallel band. Hence, when non-polarized radiation is used, Beer's law should not apply for dichroic bands of oriented samples. This effect would, therefore, tend to counteract and thus partially obscure the observed increase in absorption.

While we have been unable to confirm any of several explanations for these bands apparently caused by crystallization, at present we are inclined to consider them the result of very large intensity increases in imperceptible absorptions of the amorphous polymer. Considered from the point of view of the simple classical theory, the rate of absorption of energy from the infrared field by the absorbing structures will increase with the amplitude of vibrations in those structures. Accordingly, we might expect bands to be greatly enhanced if increasing order in the sample suppresses the processes responsible for removal of absorbed energy from the vibrating groups.

That more extensive modes of vibration should develop upon crystallization or that a recoupling of vibrating components should render infrared-active in the crystalline polymer a vibration which was inactive in the amorphous material, would imply an extension of the regions of rigidity requiring stronger forces than appear to be involved in crystallization or would imply the existence of very unlikely, unstable equilibria. A simple explanation of the appearance of the bands in terms of combination frequencies, resonance splitting, or in terms of the changes in the mutual electrostatic interaction of proximate, similar (and also similarly oriented) vibrating groups is unsatisfactory because of such factors as the sharpness of the bands and the absence of other expected components.

The differences in chemical structure between Neoprene Type CG and Type GN must be relatively small since they are not revealed by infrared. Furthermore, it is probable that the differences are only in degree, which would be revealed only by precise quantitative measurements. The spectra have not been completely elucidated but there is no evidence to indicate the presence of any 1,2- or 3,4-polychloroprene.[23] This has also been the result of an independent observation.[24] *cis*- and *trans*-2-chloro-2-butenes were examined by infrared as possible reference compounds to distinguish *cis* and *trans* structures in neoprene, but apparently were too low in chain length to serve as reference compounds, since the absorption bands were considerably shifted in many cases from their positions in the neoprene spectrum.

Acknowledgments.—The authors are indebted to their colleagues, Drs. J. R. Downing, S. L. Scott and C. J. Mighton for the initial discovery that the infrared spectra of Neoprenes Type GN and Type CG are different and to Miss Doris Huck for her assistance with the infrared measurements. Acknowledgments likewise are made to Drs. A. W. Kenney, D. M. McQueen, G. D. Patterson and B. C. Pratt for aid and encouragement and to many staff members of the Organic Chemicals Department of this Company for valuable criticisms and advice. The authors are particularly thankful to Professors R. C. Lord, F. T. Wall, J. A. Wheeler and the late A. H. Pfund for many helpful discussions.

Summary

Infrared absorption spectra of amorphous and crystalline Neoprenes Type CG and Type GN have been studied in the wave length range 2–23 microns. Spectra of polybromoprene and poly-2,3-dichloro-1,3-butadiene, the dichroism of stretched samples and spectral changes accompanying crystallization have been used to assign most of the strong bands to vibrations of more or less limited regions of the molecule. The spectra appear to be unchanged by variations in molecular weight or sol–gel relationships.

Spectral changes, some very pronounced, accompany crystallization of neoprene, either in the unstretched state or following stretching. Perceptible spectral changes were found to occur for several days following stretching of Neoprene Type GN, which crystallizes slowly. These spectral changes, particularly the surprising appearance of strong absorption bands when the polymer crystallizes, are of interest because of their relation to order in the polymer. The appearance of bands because of crystallization has been tentatively ascribed to very large intensity increases in normally imperceptible absorptions of the amorphous polymer caused by suppression in the ordered molecules of some processes responsible for dissipation of absorbed energy from the vibrations.

Wilmington, Del. Received May 5, 1949

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(23) Patat in an I. G. Report dated February 17, 1943, reported by the U. S. Technical Oil Mission, (Reel No. 53, Bag 3413, Frames 00385-00392) stated that in polycholoroprene made in emulsion at 0°, 1,2-polymers predominate but at 60°, 1,4-polymerization is most prevalent. The present authors, on the basis of results obtained in this Laboratory, cannot agree with such a hypothesis.

(24) Sheppard and Sutherland, *Faraday Soc. Discussion*, **2**, 374 (1947).