

Infrared Spectra and Crystallization of Poly-3,3-bis(chloromethyl)oxacyclobutane

MASAHIRO HATANO and SHU KAMBARA

Laboratory of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-Ku, Tokyo, Japan

INTRODUCTION

In another paper¹ we reported our study, made by standard dilatometry, of the crystallization of poly-3,3-bis(chloromethyl)oxacyclobutane. The rates of crystallization of the polymer were measured at various constant temperatures in the range of 140 to 160°C. The experimental results indicated that the rate of crystallization of the polymer might reach a maximum value in the range of 110 to 130°C.¹

In the study just completed, the crystallization characteristics of poly-3,3-bis(chloromethyl)oxacyclobutane were investigated by means of infrared spectroscopy. Previously, by infrared spectroscopy we had found that 3,3-bis(chloromethyl)oxacyclobutane was polymerized to a polyether by the catalytic reaction of boron trifluoride etherate.² The infrared spectra of 3,3-bis(chloromethyl)oxacyclobutane and its polymer are illustrated in Figure 1.² The monomer has absorption bands at 10.17 and 10.48 μ , which may be due to the skeletal vibration of the four-membered cyclic ether. The polymer obtained from the cyclic ether has no absorption bands in the region between 10.2 and 10.5 μ , whereas the same polymer has broad bands at 9.07 and 9.51 μ . The infrared spectra of the polymer were remeasured and were investigated more thoroughly in the present work than in the previous work.²

If the molecules in the polymer are all or nearly all parallel, and polarized infrared radiation is used, then the amount of absorption in some of the bands varies with the direction of vibration of the polarized radiation. The intensity of absorption with plane-polarized radiation should be a function of the angle between the direction of change of the dipole moment and the plane in which the electric vector is vibrating, and therefore a change in absorption intensity should offer some information concerning the assignment of these bands in the infrared spectra.

A comparison of the spectra obtained on oriented samples of the polymer when the electric vector was vibrating parallel to and perpendicular to the direction of extension revealed significant dichroisms in the majority of the absorption bands. The bands also showed intensity changes as the crystallization of the polymer proceeded. The crystallization process was examined by noting variations in the spectra with increase in the temperature of the specimen, the preparation of which is described in the following section, and many crystallization-sensitive bands were found. The above-mentioned dichroisms were particularly marked in the absorption bands that may be due to the rocking-mode, twisting-mode, and wagging-mode vibrations of the methylene groups in this polymer. The absorption band at 897 cm^{-1} increased markedly in intensity as crystallization of the polymer proceeded; hence this band may be regarded as a crystalline band. On the other hand, the intensity of the absorption band at 1027 cm^{-1} decreased as the crystallization proceeded, so that this band can be regarded as an amorphous band. The optical densities of these bands were observed at various temperatures during cooling of the polymer. By use of a plot of the optical densities of the bands at 897 (crystalline) and 1027 cm^{-1} (amorphous) against the temperature of the polymer, the degree of crystallinity could be measured as a function of the polymer temperature. The results were in good agreement with the results for the crystallization rate obtained dilatometrically.

Further, the polymorphism of the polymer, which had been revealed by x-ray analysis, was investigated with the use of infrared spectroanalysis. The spectra of the α and β forms of the polymer were measured, but no significant difference between them was found—only small shifts in the frequencies of the twisting-mode, wagging-mode, and rocking-mode vibrations of the methylene groups in the polymer.

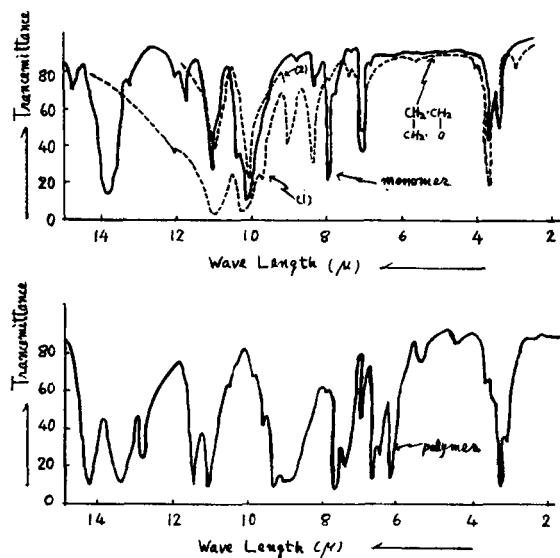


Fig. 1. Infrared spectra of top 3,3-bis(chloromethyl)-oxacyclobutane monomer and (bottom) polymer: broken lines, (1) oxacyclobutane alone, (2) 10% solution of oxacyclobutane in CCl_4 .

On the basis of deductions derived from our experimental results, we shall offer some considerations of the macromolecular structure of this polyether, poly-3,3-bis(chloromethyl)oxacyclobutane.

EXPERIMENTAL

Materials

All samples were prepared by applying the techniques used in our earlier investigation.³

Infrared Absorption Measurements

The infrared absorption measurements were carried out in a Perkin-Elmer recording spectrophotometer (Model 112; single-beam type) with the use of NaCl, KBr, and CaF_2 prisms. The dichroisms of the polymer were measured with beams of infrared radiation polarized by silver chloride plates placed immediately in front of the entrance slit of the spectrophotometer. Infrared beams, with the electric vector vibrating either parallel to or perpendicular to the extended direction of the sample, were used in the measurement of the spectra of the polyether. As the production of a highly extended and sufficiently oriented specimen of the α -polymer presented considerable practical difficulty owing to the rigidity of this material, the β -polymer was used for the production of fully extended specimens. The dichroism of fully extended ($\sim 300\%$) β -polymer was measured

in the range of 3000 to 500 cm^{-1} . In order to obtain the infrared spectra of the polymer at elevated temperatures, an 0.03-mm. film of the polymer was sealed, together with a thermocouple, between two NaCl plates, heated to above its melting point, and then cooled down to room temperature.

RESULTS AND DISCUSSION

When unpolarized radiation, which contains electric vector components vibrating in an infinite number of planes perpendicular to the direction of propagation is passed through molecules with a purely random special arrangement, interactions between any of the possible modes of vibration of the molecules and the radiation are all equally probable. In the case of a substance in which the

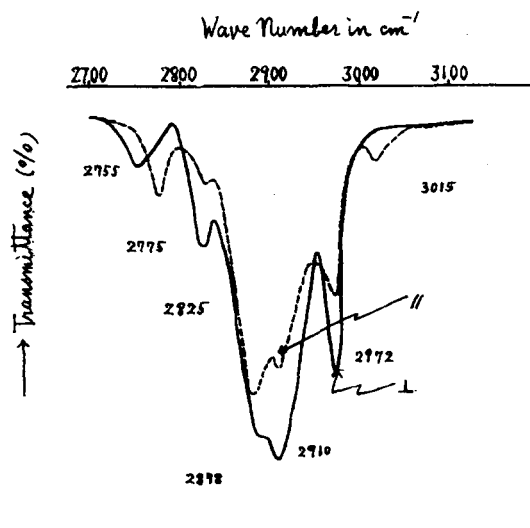


Fig. 2. Infrared dichroism of poly-3,3-bis(chloromethyl)-oxacyclobutane in the CaF_2 prism region.

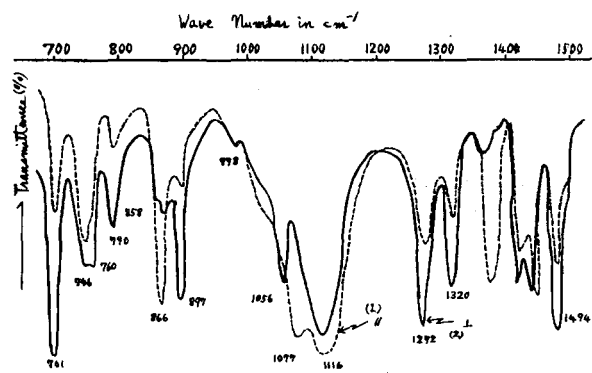


Fig. 3. Infrared dichroism of poly-3,3-bis(chloromethyl)-oxacyclobutane in the NaCl prism region.

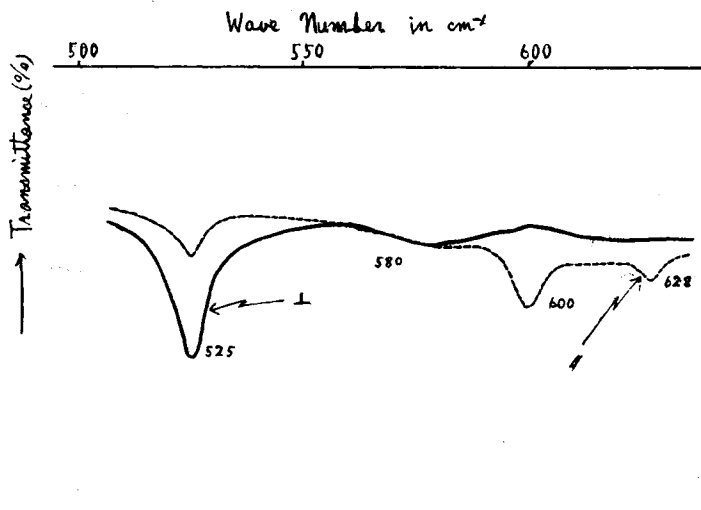


Fig. 4. Infrared dichroism of poly-3,3-bis(chloromethyl)-oxacyclobutane in the KBr prism region.

molecules are uniformly oriented, the intensity of absorption should be a function of the angle between the direction of change of the dipole moment and the plane in which the electric vector is vibrating. To take an extreme case, the absorption coefficient should be zero for those vibrations in which the change of the moment is parallel to the direction of the incident radiation. It was expected that even more detailed information about the nature of the vibrational frequencies would be forthcoming from absorption spectra obtained with plane-polarized radiation, particularly where the crystal structure had already been determined by x-ray analysis. The first recorded attempt to apply this technique to the investigation of polymers was made by Thompson, who studied the nature of the absorption band at 720 cm.^{-1} in the spectra of polyethylene.⁴ Solid polyethylene shows a doublet band at 720 cm.^{-1} which has marked dichroism and which is replaced by a single, shallower band upon melting of the polymer. Since the infrared dichroism stands in intimate relation to the orientation of molecules and to inter- or intramolecular interactions, spectra of this kind, when treated quantitatively, should supply very useful information about the crystallization process and the structure of crystalline polymers.

In the present work, the dichroisms of spectra obtained with the electric vector vibrating parallel to and perpendicular to the extended direction of this polymer may be compared in Figures 2, 3, and 4. The absorption maxima are listed in Table I with relative intensities, where the notation || means that the absorption is greater when the

TABLE I
Dichroisms and Wave Numbers of Absorption Maxima

Prism	Wave number, cm.^{-1}	Intensity ^a	Dichroism
NaCl	1494	s	⊥
	1460	s	?
	1450	s	⊥ ?
	1430	s	⊥
	1390	s	
	1375	m	⊥
	1320	s	⊥
	1272	vs	⊥
	1116	vvs	
	1077	vvs(sh)	
	1056	s	⊥
	1027	m(sh)	
	978	w(sh)	—
	897	vs	⊥
	866	vs	
	858	m(sh)	⊥
	790	s	⊥
	760	s	⊥
	746	s	⊥
	701	vs	⊥
KBr	628	m	
	600	m	
	580	w	—
CaF ₂	525	s	⊥
	2015	w	
	2972	s	⊥
	2910	vvs	⊥
	2878	vs	
	2825	m	⊥
	2775	w	
2755	w	⊥	

^a See key to abbreviations in Table III.

TABLE II
Interpretation of the Infrared Spectra of Poly-3,3-bis(chloromethyl)oxacyclobutane

Wave number, cm. ⁻¹	Relative intensity ^a	Dichroism	Character of band	Probable assignment
1390	vs		Crystalline	}CH ₂ Wagging
1375	m	⊥		
1320	vs	⊥	Crystalline	}CH ₂ Twisting
1272	vs	⊥	Crystalline	
1116	vvs			}-C-O- Stretching
1077	vvs(sh)			
1056	s	⊥		-C-C- Stretching
1027	m(sh)		Amorphous	-C-O- Stretching
978	w(sh)	—		
909	w(sh)	—		
897	vs	⊥	Crystalline	}CH ₂ Rocking
866	vs		Crystalline	
858	m(sh)	⊥		
790	s	⊥	Crystalline	
760	s	⊥		
746	s	⊥		}CCl Stretching
701	vs	⊥	Crystalline	

^a See key to abbreviation in Table III.

electric vector is parallel to the extended direction of the polymer than when it is perpendicular to it and ⊥ signifies the reverse case.

A film of poly-3,3-bis(chloromethyl)oxacyclobutane had rather larger amounts of crystallinity than the extended specimen, as found by x-ray diffraction, and when sufficiently extended it showed significant infrared dichroism in the majority of infrared absorption bands in the range between 500 and 3000 cm.⁻¹. Principally, the absorption bands at 525, 600, 701, 790, 866, 897, 1056, 1272, 1320, 1390, and 2910 cm.⁻¹ showed marked infrared dichroism. Most of these bands decreased in intensity as crystallization of this polymer proceeded, and hence these bands are considered crystallization-sensitive. On the basis of comparisons of the infrared spectra of various polyoxacyclobutane derivatives and the dichroism of the polymer studied, the assignments listed in Table II are offered tentatively for the infrared spectra of this polymer in the region of 700 to 1500 cm.⁻¹. These assignments will be discussed more thoroughly in the next paper of this series.

The absorption band at 1390 cm.⁻¹, which may be due to the wagging-mode vibration of the methylene groups, showed particularly marked dichroism parallel to the extended direction of the polymer specimen. The very strong absorption bands at 1320 and 1272 cm.⁻¹, both of which are crystallization-sensitive bands, showed nearly equal perpendicular dichroism, and one of these may be assignable to the twisting-mode vibration of the

methylene groups. The absorption bands at 1116 and 1077 cm.⁻¹, which may be due to the stretching-mode vibration of C—O bonds of the aliphatic ether type, showed weak parallel dichroism. Finally, the absorption band at 1056 cm.⁻¹, which may be due to the C—C stretching-mode vibration, and that at 897 cm.⁻¹, which may be due to the rocking-mode vibration of the methylene groups, showed particularly marked dichroism perpendicular to the extended direction of the polymer. The former was assumed to be an amorphous band because of its behavior during the melting of the polymer. The latter formed a doublet with another band at 866 cm.⁻¹ which has remarkable parallel dichroism.

The effects of crystallization on the infrared spectra of poly-3,3-bis(chloromethyl)oxacyclobutane were estimated by noting the changes in intensity of the absorption spectra with increase in the temperature of the specimen. Spectra which were measured at various constant temperatures from 23 to 230°C. are shown in Figures 5 and 6 for melting and crystallization processes, respectively. The corresponding spectral changes are listed in Table III. Since the absorption bands at 701, 790, 866, 897, 1272, 1320, and 1390 cm.⁻¹ increased markedly in intensity and their peaks shifted slightly as the crystallization proceeded, these bands were regarded as crystalline bands. On the other hand, the intensity of the absorption band at 1027 cm.⁻¹ decreased as the crystallization proceeded but increased gradually during the melting

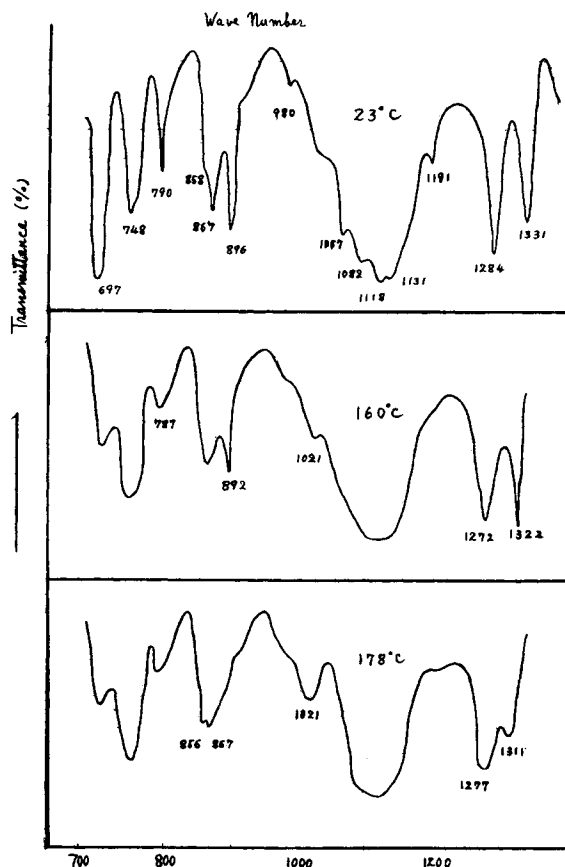


Fig. 5. Temperature dependence of the infrared spectra of the α form of poly-3,3-bis(chloromethyl)oxacyclobutane.

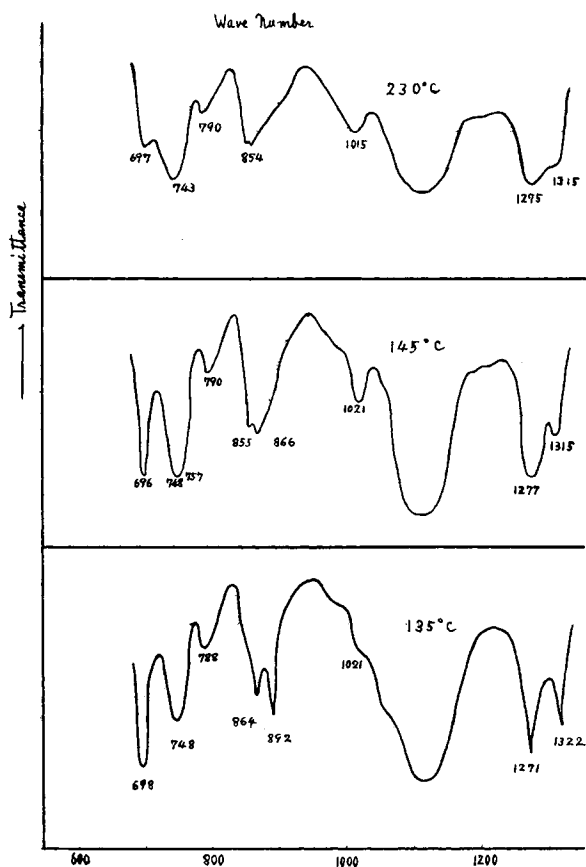


Fig. 6. Temperature dependence of the infrared spectra of the α form of poly-3,3-bis(chloromethyl)oxacyclobutane.

of the polymer, and so this band was assumed to be an amorphous band. These crystallization-sensitive bands, along with their assignments, are summarized in Table II.

Changes in the degree of crystallinity with decrease in the temperature of the polymer were measured by the use of optical densities of the two crystallization-sensitive bands at 897 and 1027 cm^{-1} . Thus, the infrared spectra of the polymer were measured at various constant temperatures in a cooling run. In this case the optical density D was defined as follows:

$$D = \log (I_0/I)$$

where I_0 is the height of the background trace at the peak of the band obtained by the baseline method, and I is the height of the band peak. The sample thickness was assumed to be constant. The optical densities of both the above-mentioned bands were plotted against the temperature of the specimen, and thus the crystallinity of the specimen could be measured as a function of the specimen

temperature. The experimental results are shown in Figure 7, and a comparison between the results obtained dilatometrically and those obtained infrared spectroscopically was made as follows. In order to estimate the apparent rate of crystallization, the reciprocals of half-value periods of the crystallization process, designated $1/t_{1/2}$ in Figure 8, were calculated from the crystallization curve obtained dilatometrically.¹ (The half-value period of the crystallization process is defined as the time sufficient for crystallization of one half of the crystallizable quantity at a given crystallization temperature.) The values of the reciprocal of $t_{1/2}$ for various samples measured at various crystallization temperatures are illustrated in Figure 8. Abrupt increases in the reciprocals of $t_{1/2}$ were observed in all samples at crystallization temperatures around 140°C. The reciprocal of $t_{1/2}$ for temperatures lower than 140°C. was too large to be measured, so that the crystallization temperature at which the $t_{1/2}$ is maximum could not be determined. Nevertheless, the experimental results of

TABLE III
 Temperature Dependence of Infrared Spectra of Poly-3,3-bis(chloromethyl)oxacyclobutane^a

Prism	β -Polymer bands at 23°C., cm. ⁻¹	Intensity	α -Polymer bands at 23°C., cm. ⁻¹	Changes in spectra with temperature (°C.) ^b					
				130	178	230	145	135	
NaCl	1390	vs	1393						
	1320	vs	1331	1322	1311(sh)	(sh)	1311, i	1322, i	
	[1280]	[m(sh)]				b			
	1272	vs	1284	1277, b	b	—	1274, i	1271, i	
	1116	vvs	1122	b	b	b	b	b	
	1077	vvs(sh)	1082	b	b	b	b	b	
	1056	vs	1057	b	b	b	b	b	
	1027	m(sh)	1025(sh)	i	si	b	s	d(sh)	
	978	w(sh)	980	d(sh)	v	—	(sh)	(sh)	
	909	w(sh)	910(sh)	vw(sh)	(sh)	(sh)	(sh)	(sh)	
	897	vs	896	d	d(sh)	v	—	si	
	866	vs	867	d	d	b	866	864	
	858	s(sh)	858	d	d	b	855	(sh)	
	790	s	790	b	b	d	i	i	
	760	s	760(sh)	b	b	b	b	b	
	746	s	748	b	b	b	b	b	
	701	vs	697	d	d	d	i	i	
	KBr	628	vw						
		600	w						
527		s							

^a Abbreviations: (sh), shoulder; s, strong; w, weak; m, medium; v, very; b, broadening; i, increase; d, decrease; v, vanished.

^b The specimen was heated and then cooled, and spectra were observed for the specimen at equilibrium at each temperature.

dilatometry indicate that the rate of crystallization might be maximum at crystallization temperatures in the range between 110 and 130°C.¹ The experimental results obtained with infrared spectroscopy, which are illustrated in Figure 7, show an abrupt increase in the crystallinity at a crystalliza-

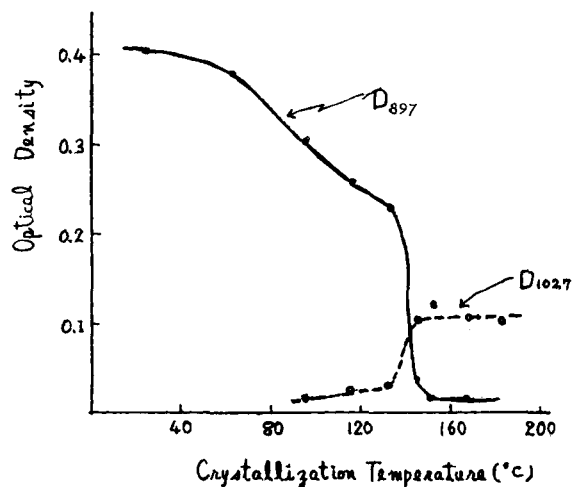


Fig. 7. Dependence of the optical densities D of the infrared absorption bands at 897 and 1027 cm.⁻¹ on the crystallization temperature.

tion temperature around 140°C. The results obtained dilatometrically, illustrated in Figure 8, and those obtained infrared spectroscopically, illustrated in Figure 7, show good agreement, as

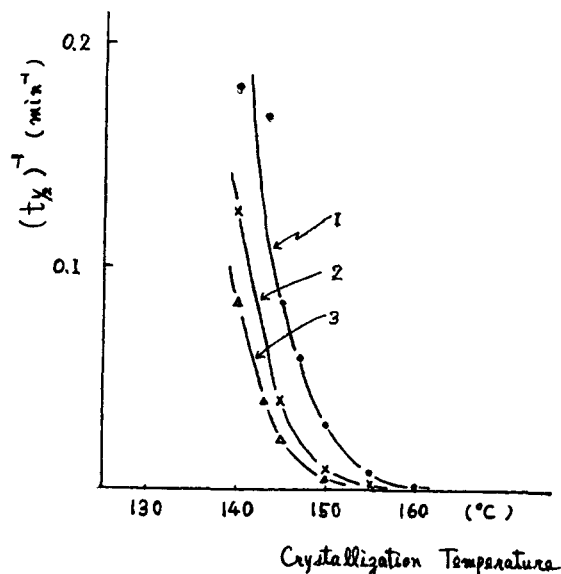


Fig. 8. Rate of crystallization vs. crystallization temperature for samples with $[\eta]$ equal to (1) 0.23, (2) 0.08, (3) 0.42.

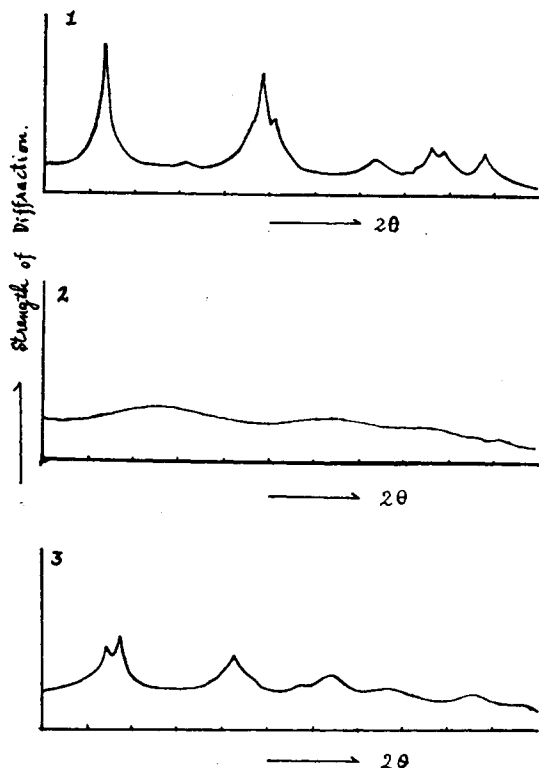


Fig. 9. X-ray diffraction diagrams for the α and β forms of poly-3,3-bis(chloromethyl)oxacyclobutane: (1) α polymer; (2) amorphous polymer (immediately after quenching); (3) β polymer.

was seen in the previous paper, and the two sets of results confirm each other.

Furthermore, the polymorphism of poly-3,3-bis(chloromethyl)oxacyclobutane, which had been found by x-ray analysis, was investigated by measurement of the infrared spectra of the α and β forms of the polymer. The spectra of both forms are listed in Table III with their relative intensities. (In the polymer obtained from 3,3-bis(chloromethyl)oxacyclobutane two crystal forms, designated α and β by Sandiford,⁵ had been revealed by their quite different x-ray diffraction diagrams.⁶) X-ray diagrams of the α and β forms of poly-3,3-bis(chloromethyl)oxacyclobutane are illustrated in Figure 9. The α form was obtained when the polymer was cooled slowly through its melting point. When it was quenched to temperatures below 0°C., on the other hand, the polymer became amorphous but then, at room temperature, it crystallized gradually to the β form. Since some relationships between the infrared spectral changes and the polymorphism of substances such as glycine⁷ had been reported, some differences between the infrared spectra, of the α and β forms of poly-

3,3-bis(chloromethyl)oxacyclobutane were expected. However, no significant differences were found—only small shifts and slight changes in intensity for the absorption bands that may be due to the wagging-mode, twisting-mode, and rocking-mode vibrations of the methylene groups in the polymer. Thus, bands at 701, 746, 1272, 1320, and 1390 cm^{-1} for the α form of the polymer corresponded, respectively, to bands at 697, 748, 1284, 1331, and 1393 cm^{-1} for the β form, with some differences in intensities.

On the basis of deductions from these experimental results, we offer the following hypothesis concerning the macromolecular structure of the polyether obtained from 3,3-bis(chloromethyl)oxacyclobutane. According to Farthing,⁸ the molten polymer can be made into film, which after cold-drawing shows a high degree of orientation, and into fiber with an identity period of 4.8 Å. The calculated period for the fully extended chain is 4.92 Å. Therefore, a macromolecule of poly-3,3-bis(chloromethyl)oxacyclobutane may twist, to some extent, around its main axis, somewhat as does polyoxymethylene. The polymorphism of the polymer may entail different angles of twist of the structure, which would result in the above-mentioned slight differences between the α and β forms.

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Synopsis

The process of crystallization and the characteristics of crystalline poly-3,3-bis(chloromethyl)oxacyclobutane were investigated by infrared spectroscopy. A comparison of the spectra obtained when the electric vector was vibrating parallel to and perpendicular to the extended direction of

specimens of this polymer showed significant dichroism in the majority of absorption bands; also, intensity changes as crystallization of the polymer proceeded were observed in both types of spectra. The crystallization process was examined by noting changes in the spectra with increase in the temperature of the polymer; many crystallization-sensitive bands were found. The dichroism was particularly marked in the absorption bands which may be due to the wagging-mode, twisting-mode, and rocking-mode vibrations of the methylene groups in this polymer. Optical densities of the bands at 1027 cm^{-1} , an amorphous band, and 897 cm^{-1} , a crystalline band, were observed at various temperatures during cooling of the polymer. By use of a plot of the optical densities of both bands against the temperature of the polymer, the degree of crystallinity of the polymer could be estimated as a function of the polymer temperature. The results are in good agreement with the dilatometric results for the crystallization rate. Also, the polymorphism of the polymer, which had been detected by x-ray analysis, was investigated by the use of infrared spectroanalysis. On the basis of deductions derived from these experimental results, we hypothesized a macromolecular structure for this polyether.

Résumé

On a étudié par spectroscopie infra-rouge la cristallisation et les caractéristiques du poly-3,3-bis(chlorométhyl)oxacyclobutane. On a comparé les spectres obtenus lorsque le vecteur électrique est perpendiculaire ou parallèle à la direction d'étirement. Ces spectres montrent un dichroïsme significatif pour la plupart des bandes du spectre infra-rouge du poly-3,3-bis(chlorométhyl)oxacyclobutane. Ces bandes d'absorption indiquent non seulement un dichroïsme significatif mais encore des changements en intensité à mesure que progresse la cristallisation du polymère. On examine cette dernière en comparant les variations du spectre avec l'augmentation de la température du polymère; on a trouvé de nombreuses bandes caractéristiques de la cristallisation dans ces spectres infra-rouges. Le dichroïsme sus-mentionné est particulièrement marqué pour les bandes d'absorption dues aux différents modes de vibration des groupements méthylène du polymère. On a observé les densités optiques de la bande de 1027 cm^{-1} (bande amorphe) et à 897 cm^{-1} (bande cristalline) à différentes températures. On a porté

en graphique la densité optique des deux bandes en fonction de la température, ce que a permis de mesurer la cristallinité du polymère en fonction de ces données. Ces résultats sont en bon accord avec ceux obtenus par dilatométrie. On a pu étudier par analyse infra-rouge le polymorphisme du polymère mis en évidence par la diffraction des rayons-X. Sur la base de certaines déductions faites à partir des résultats expérimentaux, nous avons émis certaines considérations au sujet de la structure de ce polyéther.

Zusammenfassung

Die Kristallisationsphänomene und -charakteristik von Poly-3,3-bis(chloromethyl)oxacyclobutan wurden durch Infrarotspektroskopie untersucht. Ein Vergleich der Spektren mit elektrischem Vektor parallel und senkrecht zur Dehnungsrichtung zeigte bei der Mehrzahl der Absorptionsbanden des Infrarotspektrums von Poly-3,3-bis(chloromethyl)oxacyclobutan einen charakteristischen Dichroismus. Diese Absorptionsbanden zeigten nicht nur Dichroismus sondern auch Intensitätsänderungen bei fortschreitender Kristallisation des Polymeren. Die letztere wurde durch Vergleich mit der Abhängigkeit der Spektren von der Temperaturzunahme des Polymeren geprüft; es wurden in den Infrarotabsorptionsspektren viele kristallisationsempfindliche Banden gefunden. Der oben erwähnte Dichroismus war besonders für diejenigen Absorptionsbanden ausgeprägt, welche möglicherweise auf wagging-, twisting- oder rocking-Frequenzen der Methylengruppen in diesem Polymeren zurückgeführt werden können. Die optische Dichte der Banden bei 1027 cm^{-1} , einer amorphen Bande, und bei 897 cm^{-1} , einer kristallinen Bande, wurde bei verschiedenen Temperaturen während einer Abkühlung dieses Polymeren beobachtet. Durch Auftragen der optischen Dichte beider Banden gegen die Temperatur des Polymeren, wurde der Kristallinitätsgrad als Temperaturfunktion bestimmt. Die Ergebnisse standen mit den dilatometrisch für die Kristallisationsgeschwindigkeit erhaltenen in guter Übereinstimmung. Auch die röntgenographisch gefundene Polymorphie des Polymeren wurde mittels Infrarotspektroskopie untersucht. Auf der Grundlage der Schlussfolgerungen aus einigen experimentellen Ergebnissen werden Betrachtungen über die Molekülstruktur dieses Polyäthers angestellt.

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