relaxation strength, *i.e.*, the T_1 and $T_{1\rho}$ minima are shallower. Owing to incomplete deacetylation of the original PVAc, about 10% CH_3 groups remain. We ascribe the remanent relaxation, Figure 6, to these CH_3 groups. This result is consistent with the tunneling mechanism but less conclusive than we had hoped.

(C) Other Relaxations. In some specimens of PVAc, a T_1 minimum is observed in the neighborhood of −60°, and $T_{1\rho}$ is affected near −130°. High-resolution nmr spectra reveal the presence of an impurity in these specimens. It is likely that the impurity is copolymerized and contains a methoxy group. A dynamic mechanical loss maximum reported[10] near −100° at 2×10^6 Hz may also be due to this impurity.

Acknowledgments. We are indebted to Mr. G. H. Williams for aid in obtaining the polymer specimens. Mr. J. J. Ryan assisted in connection with deuteration of the PVAc.

Conformational Structure and Vibrational Spectra of Poly(methyl methacrylate) and of Its Models

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ABSTRACT: By analysis of vibrational spectra of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid, the stable conformers of this most simple model of poly(methyl methacrylate) have been determined. Vibrational spectra and conformational structure of crystalline and amorphous poly(methyl methacrylate) and of the stereo complex are discussed on the basis of known conformational structures of model compounds.

The conformational structure of crystalline poly(methyl methacrylate) (PMMA) was investigated theoretically[1,2] and by X-ray diffraction.[2–4] By the latter method, helical structure with 5_1 and 5_2 helices was observed in crystalline isotactic PMMA. For syndiotactic PMMA, a complete X-ray analysis has not been performed so far. Only in the stereo complex (iso:syndio = 1:2) a structure of the syndiotactic sequences has been proposed by Liquori,[5] based on X-ray analysis. This structure was criticized by Gotlib[1] on the basis of a theoretical analysis of conformer energies.

In all these studies, the conformation of amorphous PMMA has not been considered, and even the conformation of syndiotactic dyads in the crystalline polymer has not been determined unequivocally. In this paper, we have attempted to determine the conformational structure of PMMA from infrared spectra of the polymer, based on a study of its simplest model—the dimethyl ester of 2,2,4,4-tetramethylglutaric acid (DMTG). In addition to DMTG, we also analyzed some of its deuterio derivatives [the dimethyl ester of 2,2,4,4-tetramethylglutaric-*3*-d_1 acid (DMTG–CHD) and the dimethyl-d_1 ester of 2,2,4,4-tetramethylglutaric acid (DMTG–$COOCH_2D$)] and the methyl ester of 2,2,4,4-tetramethylvaleric acid. From the knowledge of the stable conformers of DMTG and their infrared spectra, we have attempted to elucidate the conformational structure of dyads in PMMA.

Experimental Section

Synthesis of Models. Methyl 2,2,4,4-tetramethylvalerate was prepared by esterification of 2,2,4,4-tetramethylvaleric acid by diazomethane. The acid was prepared by carbonization of 1,3,3-trimethylpentylmagnesium chloride[6] with solid CO_2. The trimethylpentyl chloride was obtained by addition of HCl to diisobutylene.[7]

Dimethyl 2,2,4,4-tetramethylglutarate[8] was prepared from diethyl 3-hydroxy-2,2,4,4-tetramethylglutarate, obtained by the Reformatski reaction of ethyl 2-bromoisobutyrate with ethyl formate. After hydrolysis, the free acid was reduced with HI to tetramethylglutaric acid which was esterified by diazomethane.

Di(methyl-d_1) 2,2,4,4-tetramethylglutarate[8] was prepared by addition of diazomethane to tetramethylglutaric-d_2 acid; this was obtained from tetramethylglutaric acid by isotopic exchange with excess D_2O.

Dimethyl 2,2,4,4-tetramethylglutarate-*3*-d_1[8] was obtained by an analogous method as dimethyl 2,2,4,4-tetramethylglutarate; the ethyl formate-*1*-*d* was obtained from formic acid d_2 (Merck AG) and ethanol-d_1 (Isocommerz).

The chemical purity of all these compounds was controlled by physical constants, elementary analysis, and infrared spectra, and was better than 99.9%. The isotopic purity of the deuterated compounds was determined by nmr spectra: DMTG–$COOCH_2D$, 65%; DMTG–CHD, 100%.

Polymers. The tacticity of the PMMA samples was determined by nmr spectra:[9] syndiotactic PMMA (85% S, 15% H, 0% I), isotactic PMMA (0% S, 2% H, 98% I). The stereo complex (iso:syndio = 1:2) was prepared from a solution of PMMA in acetonitrile.[5]

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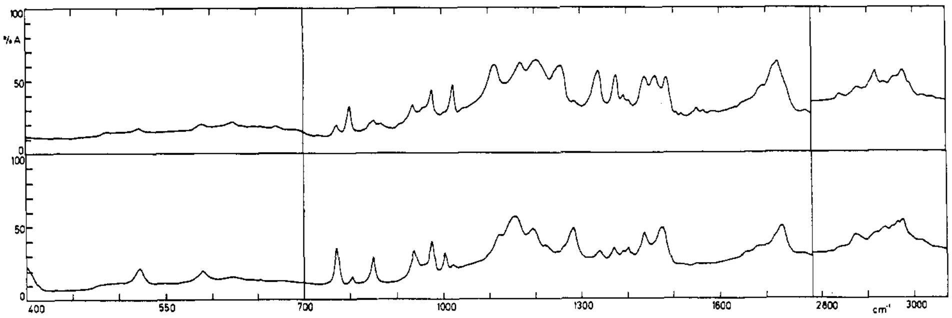

Figure 1. Infrared spectra of oriented crystals of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid.

Spectral Measurements. Infrared spectra were measured in the range 400–3500 cm^{-1} on the Zeiss UR 10 spectrometer. Dichroism of the bands was measured by means of a Zeiss AgCl polarizer.

Results and Discussion

Structure of Model Compounds. If only staggered conformers are considered, then the dimethyl ester of 2,2,4,4-tetramethylglutaric acid (DMTG) can form four different conformations of the carbon skeleton. In addition to rotations about skeletal C–C bonds, further conformers can be formed by rotations about the C–C bond connecting the ester and about ester C–O bonds. Based on the results of Wilmshurst[10] and of other authors,[11,12] only the cis form of the ester groups has been considered in all the compounds investigated in this study. Similarly, on the basis of our paper[13] on the conformational structure of methyl esters of aliphatic acids, only the conformers with a syn orientation of the C=O bond with respect to methyl or methylene are supposed to be formed by rotation about the C—C bond connecting the ester group.

Oriented crystals of DMTG exhibit a pronounced dichroism in the infrared spectra (Figure 1), indicating the presence of only one conformer in the crystals of DMTG. The structure of this conformer was determined by comparison of the dichroism of DMTG with the dichroism of the oriented crystals of 2,4-dichloro-2,4-dimethylpentane.[14] As seen from Table I, the bands of C–CH$_3$ bending and rocking vibrations in both these compounds exhibit the same dichroism and therefore both these compounds must have the same structure of the carbon skeleton. In 2,4-dichloro-2,4-dimethylpentane, the structure in the crystalline state was determined in our previous papers[14,15] from analysis of C–Cl stretching vibrations. DMGT must therefore have an analogous structure, which is indicated in Figure 2 (I).

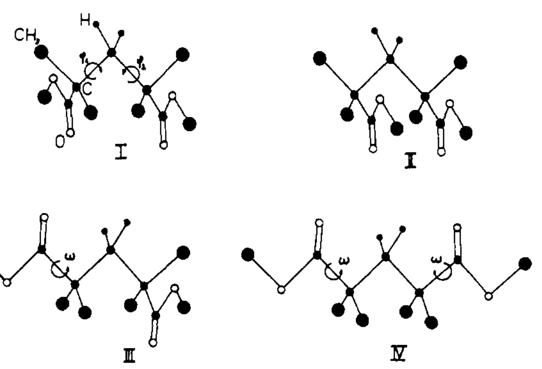

Figure 2. Conformational structures of DMTG.

In infrared spectra of liquid DMTG, the intensities of some bands differ from those observed in the solid state (Figure 3); pronounced intensity differences are observed especially in the range 1100–1300 cm^{-1}. A new band appears at 868 cm^{-1}, whereas the intensity of the band at 848 cm^{-1} is decreased. This indicates the presence of further conformers in the liquid state. Bands at 868 and 848 cm^{-1} also appear in infrared spectra of liquid DMTG–COOCH$_2$D (Figure 4a). In the infrared spectrum of DMTG–CHD (Figure 4b), the bands at 868 and 848 cm^{-1} shift to lower values. Because of this behavior, these bands are assigned as CH$_2$ rocking vibrations interacting with the carbon skeleton. This shows that the additional conformer appearing in the liquid state differs from the above-mentioned solid-state conformer by rotation about a skeletal C–C bond.

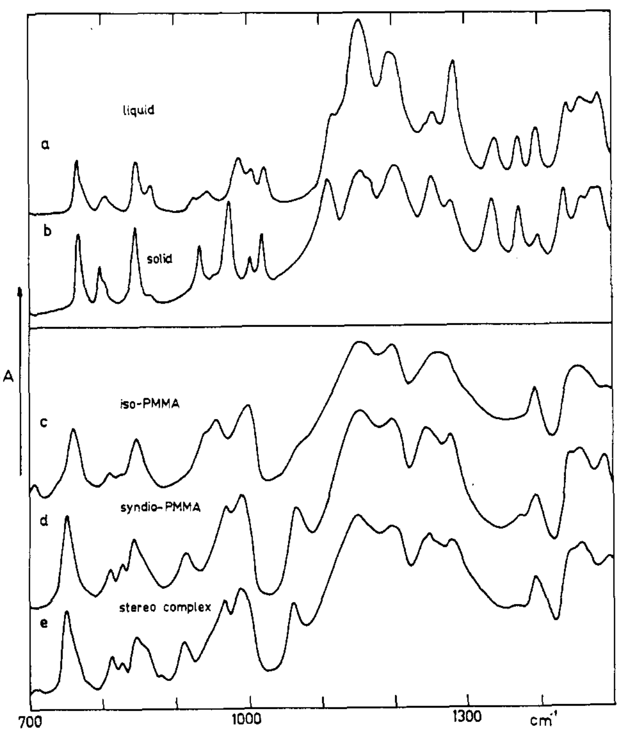

Figure 3. Infrared spectra of DMTG and PMMA: (a) liquid DMTG, (b) solid DMTG, (c) isotactic PMMA, (d) syndiotactic PMMA, (e) stereo complex.

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TABLE I

DICHROISM OF BANDS OF SYMMETRICAL BENDING AND ROCKING VIBRATIONS OF C–CH_3 GROUPS IN 2,4-DICHLORO-2,4-DIMETHYLPENTANE, DMTG, DMTG–CHD, AND DMTG–$COOCH_2D$

	Rock(C–CH_3)		Bending(C–CH_3)							
Substance	Frequency, cm^{-1}	*I*	Frequency, cm^{-1}	*I*	Frequency, cm^{-1}	*I*	Frequency, cm^{-1}	*I*	Frequency, cm^{-1}	*I*
2,4-Dichloro-2,4-dimethylpentane	902 (σ)	s	1365 (σ)	m	1378 (π)	s	1396 (π)	m	1400 (σ)	wsh
DMTG	936 (σ)	m	1370 (σ)	sh	1376 (π)	s	1392 (π)	sh	1402 (σ)	w
DMTG–CHD	938 (σ)	w	1371 (σ)	m	1380 (π)	wsh	1395 (τ)	m	1403 (σ)	wsh
DMTG–$COOCH_2D$	936 (σ)	m	1370 (σ)	sh	1374 (π)	m	1396 (π)	sh	1402 (σ)	w

In order to determine which of the possible conformations of the skeleton exist in liquid DMTG, we also studied the structure of the methyl ester of 2,2,4,4-tetramethylvaleric acid, which can form only two different skeletal conformations (Figure 5). On transition from the liquid to the solid state, no lines are observed to "freeze out" in this compound (Figure 6). We therefore assume that in the dimethyl ester of 2,2,4,4-tetramethylvaleric acid this band shifts to lower wave numbers and is overlapped by the band at 981 cm^{-1}.

In conformer V (Figure 5), rotation about the ester C–C bond is improbable, because only one position of the ester group is free of steric hindrance. In form VI, rotation about the ester C–C bond can proceed without any steric hindrance. For this reason, both the conformer with the syn position of the C=O bond with respect to methyl and the conformer with the C=O bond syn to methylene can exist. The equilibrium between these two forms would have to change at crystallization and with temperature changes in the liquid state, and this would have to be observed in the spectra. As no such changes are observed, we assume that both in the solid and in the liquid state only the conformer V is present in the methyl ester of 2,2,4,4-tetramethylvaleric acid. This conformation of the skeleton is also the most stable form of the analogous chlorine compound.[14]

In conformer VI of 2,2,4,4-tetramethylvaleric acid, four methyl groups are in close contact, similarly as in form IV of DMTG (Figure 2). As it is not possible to detect conformer VI of 2,2,4,4-tetramethylvaleric acid experimentally, we assume that form IV of DMTG will be also disfavored and will not be present in liquid DMTG. Similarly as in conformer V of the methyl ester of 2,2,4,4-tetramethylvaleric acid, in conformer II of DMTG rotation about the ester C—C bond is improbable; from this it follows that the C=O bonds in the 1,3 positions would have to be parallel. However, the carbonyls are polar groups, and their mutual interaction probably excludes a parallel orientation in 1,3 positions similarly as parallel Cl atoms in 1,3 positions are excluded in halogenated paraffins;[16] consequently, we assume this form to be energetically disfavored. Liquid DMTG is therefore expected to contain form III (Figure 2) in addition to form I occurring in the solid state.

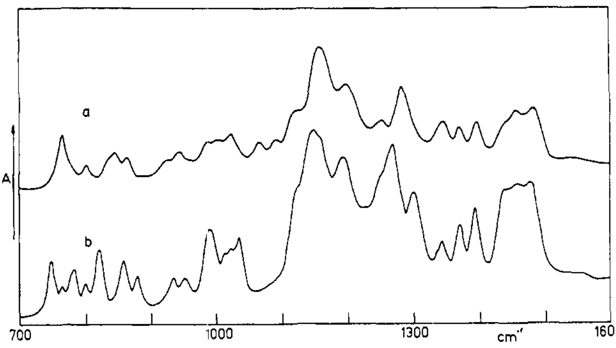

Figure 4. Infrared spectra of deuterio derivatives of DMTG: (a) liquid DMTG-$COOCH_2D$, (b) liquid DMTG-CHD.

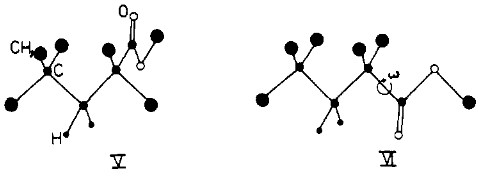

Figure 5. Conformational structures of 2,2,4,4-tetramethylvaleric acid.

In conformer III of DMTG, one ester group can exist in two conformations. In one, the C=O bond is in a syn position with respect to the methyl, and in the other it is in a syn position with respect to the methylene. The change of equilibrium concentrations of these two forms is exhibited by a change of the intensities of ester group bands in the range 1100–1300 cm^{-1} upon transition from solid to liquid state.

In our study of conformational forms of DMTG and other model compounds, we cannot determine how closely staggered forms approximate the real structure, because small deviations of the angles φ_1 and φ_2 (Figure 2) cannot be detected from infrared spectra.

Conformational Structure of PMMA. If only staggered forms are assumed, and rotation of ester groups is not considered, six different conformations can occur in isotactic PMMA and six in syndiotactic PMMA dyads. It is well

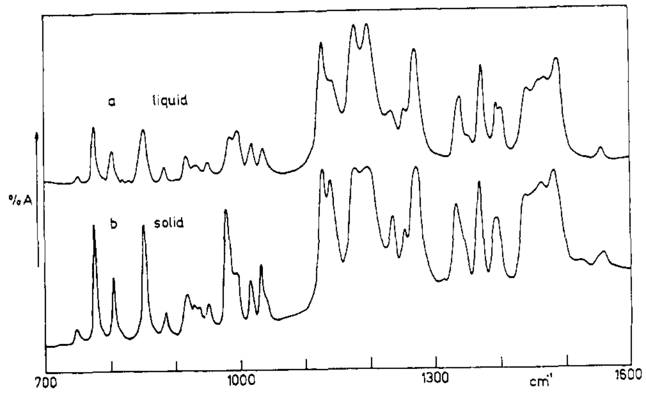

Figure 6. Infrared spectra of 2,2,4,4-tetramethylvaleric acid: (a) liquid, (b) solid.

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known[17–21] that conformational forms found in dimer models of vinyl polymers agree with the forms occurring in the dyads of the corresponding polymers. Moreover, the most stable conformer of the dimer model usually is identical with the dyad conformation observed in the crystalline polymer. We therefore assume that also in PMMA only the dyad conformations corresponding to structures I and III of DMTG can occur, and that in crystalline isotactic and syndiotactic PMMA structure I of DMTG will be present (Figure 1).

This dyad conformation would correspond to the 3_1 helix in crystalline isotactic PMMA and to a planar zigzag chain in crystalline syndiotactic PMMA. In the helices 5_1 and 5_2 found in isotactic PMMA by X-ray diffraction,[2–5] dyad conformations differ from form I of DMTG by a shift of the angles φ_1 and φ_2 by 10–15° from the staggered values. Because the values of the angles φ_1 and φ_2 cannot be determined accurately from infrared spectra, it can be stated that the proposed structure of crystalline isotactic PMMA does not contradict the structure derived from X-ray analysis. For the same reason the chain in crystalline syndiotactic PMMA need not be strictly planar, even if the dyad structure does approximately correspond to form I of DMTG.

If only conformers analogous to the structures found in model compounds are assumed to exist in PMMA, then the ester groups should always be oriented syn with respect to the α-methyl group. This position of the ester group agrees with the structure of PMMA as proposed by Liquori[3] and Gotlib.[1] It differs from one of the structures considered by Tadokoro.[2]

Similarly as in DMTG, also in PMMA conformation-sensitive bands appear at 860 and 840 cm^{-1}. The band at 860 cm^{-1} which corresponds to the band at 868 cm^{-1} in form III of DMTG is absent in crystalline syndiotactic and isotactic PMMA, but it is weakly indicated in amorphous PMMA.[22] The band at 840 cm^{-1}, corresponding to the band at 848 cm^{-1} in form I of DMTG, is very strong in the crystalline polymers. This indicates that in amorphous isotactic and syndiotactic PMMA, there occurs a small amount of the dyad corresponding to form III of DMTG. Infrared spectra confirm that the structure of dyads in crystalline isotactic and syndiotactic PMMA corresponds to form I of crystalline DMTG. The amount of the conformer occurring in small amounts in amorphous PMMA increases considerably in the stereo complex (iso:syndio = 1:2). Formation of the complex is probably connected with a rotation about skeletal C—C bonds, and dyads with structure III appear.

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Synthesis and Optical Properties of Asymmetric Polyamides Derived from Optically Active Cyclic Dicarboxylic Acids[1,2]

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ABSTRACT: Optically active dicarboxylic acids, (+)-(*S*)- and (−)-(*R*)-*trans*-1,2-cyclopropanedicarboxylic acids (1,2-C3), (−)-(*R*)-*trans*-1,2-cyclobutanedicarboxylic acid (1,2-C4), (+)- and (−)-*trans*-1,3-cyclopentanedicarboxylic acids (1,3-C5), and polyamides composed of these diacids and secondary diamines such as *trans*-2,5-dimethylpiperazine (DMPIP), piperazine (PIP), or *N,N′*-dimethylethylenediamine (DMED) have been prepared. Diamide model compounds composed of the diacids and piperidine have also been prepared. Optical properties and conformations of these polyamides and diamide model compounds in various solvents have been investigated by means of optical rotatory dispersion (ORD) and circular dichroism (CD). The results, together with previous data, suggest that the rigid DMPIP and PIP polyamides exist in some ordered conformations in 2,2,2-trifluoroethanol (TFE) and tetramethylenesulfone (TMS), allowing coupling of the amide chromophores along the polymer chains. On the contrary, the flexible open-chain DMED polyamides have an unordered conformation in solution. The DMPIP and PIP polyamides in methanesulfonic acid (MSA) exhibit quite different ORD/CD spectra than in TFE and TMS. In particular, for the case of the 1,2-C3·DMPIP and PIP polyamides, it has been suggested that some conformational transition may take place on going from TFE or TMS to MSA.

Over the past decade, the conformational behavior of synthetic polypeptides in solution has been intensively studied to help elucidate that of the more complex structure of proteins and enzymes. However, relatively little attention has been given to the optical properties and the conformations of other synthetic optically active condensation polymers.

When a polyamide is composed of conformationally rigid monomer units, portions of the polyamide chain may have an ordered conformation which can allow coupling of identical nonconjugated amide chromophores.[3] Thus, it may be expected that such a polyamide would exhibit some of the

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(1) This is the 23rd in a series of papers concerned with the synthesis and properties of asymmetric polymers.

(2) For the previous paper in this series, see C. G. Overberger, A. Ohnishi, and A. S. Gomes, *J. Polym. Sci., Part A-1*, in press.

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