Vibrational spectra and normal-coordinate analysis of poly(3,3-dimethyloxetane)

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The infra-red and Raman spectra of the two stable polymorphic forms of poly(3,3-dimethyloxetane) are presented. Normal-coordinate treatments have been performed on molecular models of both crystalline modifications. The agreement between the observed and calculated frequencies was excellent, and the assignment of the normal modes was satisfactorily realized. The vibrational region most sensitive to the molecular configuration is also analysed.

(**Keywords:** Raman spectra; infra-red spectra; normal-coordinate analysis; polyethers; poly(3,3-dimethyloxetane); crystalline conformers)

INTRODUCTION

Polyoxetanes are a type of polyether with general structure (–O–CH$_2$–CR$_1$R$_2$–CH$_2$–). Substitution of R$_1$R$_2$ by alkyl groups introduces important modifications in their properties. At the moment only a few papers on the structure[1–4], thermal behaviour[5,6] and crystallinity[7–10] of these branched polyoxetanes have been published.

The branched polyether series generally have a variety of conformational forms, which lead to various crystalline structures. In previous work[4–10], a strong dependence of the crystalline form of these polyethers on external physical variables (temperature, stretch, pressure) has been observed, and consequently conformational characterization of the conformers was necessary.

Vibrational spectroscopy is a potentially useful tool for deriving information on conformational variations[11]. This technique involves measurements of infra-red and Raman spectra and their analysis, most often incorporated with a normal-coordinate treatment. While linear polyethers have been the subject of numerous spectroscopic studies[1,12–14], these analyses and a satisfactory interpretation of the vibrational spectra of branched polyethers are still missing. The most obvious difficulty is the size of the problem, because the relatively large repeat unit results in a complicated spectrum.

The main purpose of this paper is to realize a vibrational characterization of two crystalline forms of poly(3,3-dimethyloxetane) (PDMO), corresponding to substitution of R$_1$ and R$_2$ by methyl groups. In a previous paper[8], it has been shown that PDMO can exist in three different crystalline phases, but when isothermal crystallization is used, only modifications II and III were obtained. Modification I is a planar zig-zag conformation and is only present in combination with modification II maintaining the sample stretched[2]. The preferred chain conformations in the main crystalline variations are $T_3GT_3\bar{G}$ with monoclinic structure (modification II) and $(T_2G_2)_2$ with orthorhombic structure (modification III).

For the two conformers of poly(3,3-dimethyloxetane) it may reasonably be expected that vibrational spectra will show noticeable differences. On this basis, we have succeeded in analysing[4,7,10] the evolution of these crystalline forms with various parameters (crystallization temperature, annealing temperature, pressure, etc.) based on spectral differences.

The optimum assignment of observed frequencies, together with their changes as a function of conformational state, is based on a normal-coordinate analysis. In this way, the majority of the force constants used were transferred from the valence force field (VFF) basis of the Snyder[15] and Brooks and Haas[16] studies. The results obtained here will be used to analyse other branched polyethers in order to get more complete knowledge of the vibrational spectra, which will allow conformational characterization of the different crystal modifications appearing in these polymers. Bearing in mind the relatively small amount of information we possess about the force field available for this complex molecule, we propose this study as a first stage in the conformational characterization of these branched polyethers.

EXPERIMENTAL

The PDMO samples used in this study have been described previously[4]. The method essentially consists of crystallization of the polymer above 16°C (modification II) or below 0°C (modification III). Thus, the samples were prepared by moulding the polymer at temperatures higher than the melting point (75°C), followed by crystallization by rapid cooling at 20°C or −10°C. To avoid the presence of form II during crystallization of modification III, the molten sample was quenched to

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−50°C and thereafter crystallized at −10°C. All samples for infra-red analysis were prepared as films.

Raman spectra were obtained on a Jobin–Yvon Ramanor HG2S spectrometer. The 514.5 nm exciting line of an argon-ion laser was utilized as the source of illumination. The laser power was approximately 150 mW at the sample. A scan speed of $20\,\mathrm{cm^{-1}\,min^{-1}}$ was used and the monochromator slit width was fixed at 250 μm. The spectrometer was interfaced via a Microlink (Biodata) to a Commodore microcomputer. The computer allows for multiple scans, thus improving the signal-to-noise ratio of the final spectrum. Infra-red spectra were recorded using a Nicolet FTIR 60SX with a resolution of $1\,\mathrm{cm^{-1}}$ and 50 scans.

NORMAL-COORDINATE ANALYSIS

The crystal structures of two main crystalline modifications of PDMO have been determined by Takahashi *et al.*[2] from X-ray diffraction studies. In modification II, two chains in $T_3GT_3\bar{G}$ conformation pass through a monoclinic cell with parameters $a=8.93$ Å, $b=7.48$ Å, c (fibre axis) $=8.35$ Å, $\beta=97.9°$ and space group $P2_1/c$ (C^5_{2h}). In modification III, two T_2G_2 chains pass through an orthorhombic cell with parameters $a=15.6$ Å, $b=5.74$ Å, c (fibre axis) $=6.51$ Å and space group $C222_1$ (D^5_2).

The symmetry operations of the isolated molecular chain belong to the factor group isomorphous to the point group C_s for conformation II, and to D_2 for conformation III[2]. The results of the factor group analysis show that the normal modes (excluding pure translations and rotation) can be classified into the following irreducible representations: modification II—46 A′, 46 A″; modification III—23 A, 23 B_1, 23 B_2, 23 B_3. We have previously demonstrated[10] that only modification II can be present after a strong stretching of the sample. Thus, only the polarized spectra of the crystallized samples with this crystalline conformation can be analysed.

To calculate the normal coordinates, the concept of isolated polymer chain was applied. No splitting into doublets due to the effect of interactions between two chains contained in the unit cell was observed. To try to observe the splitting, the spectra of the cooled samples were recorded, showing no important differences between the spectra at different temperatures, possibly due to a very weak interaction between the molecular chains as a consequence of the presence of branches.

Normal-coordinate calculations of linear polyethers have been performed by Tadokoro *et al.*[17–20] using a modified Urey–Bradley force field (MUBFF). However, this type of force field is shown to be inappropriate to the study of conformational disorder[21,22]. Consequently, in our study we must use a valence force field type (SGVFF)[23–27].

The normal coordinates were calculated on a VAX–VSM computer, using an adaptation for polymers of a program described previously[28]. The modification of the original program is based on the calculation method detailed by Hannon *et al.*[29]. The necessary data for the calculation consist of Cartesian coordinates and atomic masses, internal coordinates, force constants and observed frequencies (necessary for a force-constant refinement).

The Cartesian coordinates for an isolated chain in a preferred conformation of the two crystalline forms were calculated with a CART program[30], using the molecular parameters shown in *Table 1*. The results appear in *Tables 2* and *3*. In *Figures 1* and *2* are illustrated the conformations of the two modifications and the description of the internal coordinates (105 for modifications II and III) for conformer III, with the exception of the torsional modes. The internal coordinates are identical for the two conformers. The resulting force field contains 41 types of force constants, and their definitions in terms of internal coordinates and values are listed in *Tables 4* and *5*, using the usual nomenclature[23–27,31]. In *Table 5* are presented only the

Table 1 Molecular parameters of poly(3,3-dimethyloxetane)

Parameter	Modification II	Modification III
Bond lengths (Å)	C–C: 1.54 C–O: 1.43 C–H: 1.09	C–C: 1.54 C–O: 1.43 C–H: 1.09
Valence bond angles (deg)	C1C2C3: 107.2 C5O4O3: 107.2 C5O6C7: 107.2 Other angles: 109.47	All angles: 109.47
Internal rotation angles (deg)	C1C2C3O4: 179 C2C3O4C5: 179 C5C6C7O8: 179 Other angles: 180	All angles: 180

Table 2 Cartesian coordinates of the atoms in modification II of poly(3,3-dimethyloxetane) (in Å)

Atom	x	y	z
C1	1.192	0.007	−2.174
C2	1.257	−0.513	−0.726
C3	0	0	0
O4	0	−0.477	1.348
C5	−1.192	0.007	1.974
C6	−1.257	−0.513	3.422
C7	0	0	4.148
O8	0	−0.477	5.496
C9	2.515	0	0
C10	1.257	−2.053	−0.726
C11	−2.515	0	4.148
C12	−1.257	−2.053	3.422
H13	1.192	1.096	−2.168
H14	2.068	−0.333	−2.723
H15	0	1.090	0
H16	−0.890	−0.363	−0.514
H17	−1.192	1.096	1.980
H18	−2.068	−0.333	1.425
H19	0	1.090	4.148
H20	0.890	−0.363	3.634
H21	2.515	−0.363	1.028
H22	3.405	−0.363	−0.514
H23	2.515	1.090	0
H24	1.257	−2.417	0.302
H25	0.367	−2.417	−1.240
H26	2.147	−2.417	−1.240
H27	−2.515	−0.363	5.176
H28	−2.515	1.090	4.148
H29	−3.405	−0.363	3.634
H30	−1.257	−2.417	4.450
H31	−2.147	−2.417	2.908
H32	−0.367	−2.417	2.908
O33	0	−0.477	−2.800
C34	1.192	0.007	6.122
C35	0	0	−4.148

Table 3 Cartesian coordinates of the atoms in modification III of poly(3,3-dimethyloxetane) (in Å)

Atom	*x*	*y*	*z*
C1	−1.257	1.778	1.257
C2	−1.257	0.889	0
C3	0	0	0
O4	1.168	0.826	0
C5	2.335	0	0
C6	3.593	0.889	0
C7	3.593	1.778	−1.257
O8	3.593	0.953	−2.425
C9	−2.514	0	0
C10	−1.257	1.778	−1.257
C11	4.840	0	0
C12	3.593	1.778	1.257
H13	−2.147	2.408	1.257
H14	−0.367	2.408	1.257
H15	0	−0.629	0.900
H16	0	−0.629	−0.890
H17	2.335	−0.629	0.890
H18	2.335	−0.629	−0.890
H19	2.703	2.408	−1.257
H20	4.483	2.408	−1.257
H21	3.405	0.629	0
H22	−2.515	−0.629	−0.890
H23	−2.525	−0.629	0.890
H24	−0.367	2.408	−1.257
H25	−1.257	1.149	−2.147
H26	−2.147	2.408	−1.257
H27	5.740	0.629	0
H28	4.850	−0.629	0.890
H29	4.850	−0.629	−0.890
H30	4.483	2.408	1.257
H31	2.703	2.408	1.257
H32	3.593	1.149	2.147
O33	−1.257	0.953	2.425
C34	−1.257	1.778	3.593
C35	3.593	1.778	−3.593

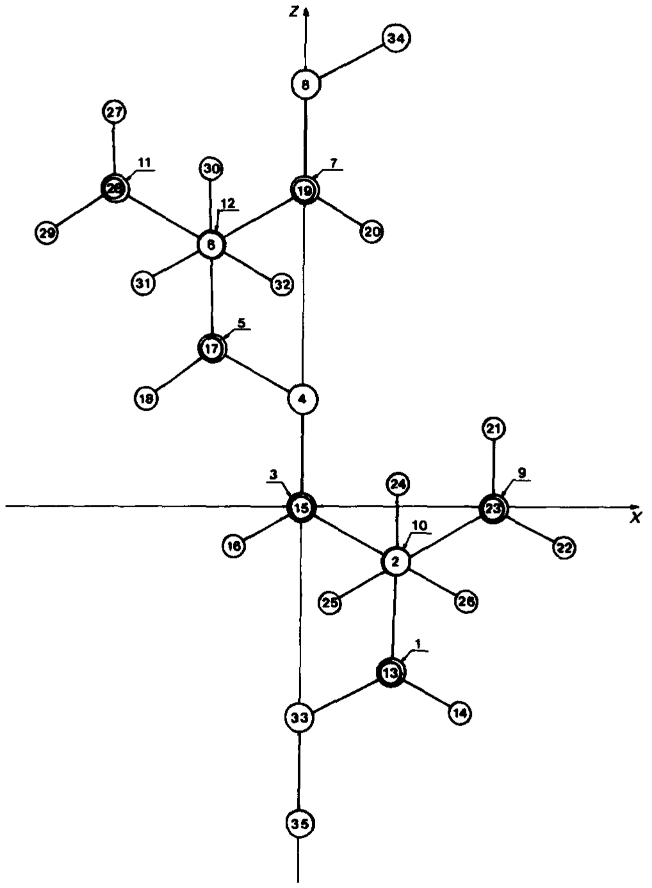

Figure 1 Numbered chemical repeat unit of poly(3,3-dimethyloxetane) in conformation II

force constants for conformation III with different definition of internal coordinates in relation to form II. The asterisks appearing in *Table 4* indicate the force constants used in the refinement process, which seem the most specific of these molecules with respect to the quoted references.

RESULTS AND DISCUSSION

As previously described, only the sample with crystalline variation II can be totally stretched and therefore the polarized spectra of this conformer were registered. Raman spectra of a highly drawn semicrystalline sample of poly(3,3-dimethyloxetane) (form II) obtained according to the scattering geometry depicted in *Figure 3* are shown in *Figures 4a–d*. The notation for each Raman spectrum describes its scattering geometry[32].

The geometry analysis of the T_3GT_3G conformation (form II) of PDMO is shown in *Table 6*, indicating that the bands with preferent polarization $x(zz)y$ belong to the symmetry type A′, while on the other spectra the bands corresponding to the two types of symmetry A′ and A″ appear together.

In *Figure 5* is presented the Raman spectrum of the sample crystallized in form III. The Raman spectrum of PDMO in the amorphous state is also registered (*Figure 6*) and was obtained by heating the sample above the melting point, maintaining this temperature for 1 h with a later quenching process to −195°C, and finally recording the spectrum in a special cell[33]. In *Figures 7* and *8* the infra-red spectra of the two conformers are presented.

The observed and calculated wavenumbers and the approximate potential energy distribution for the two conformations of PDMO are listed in *Tables 7* and *8*.

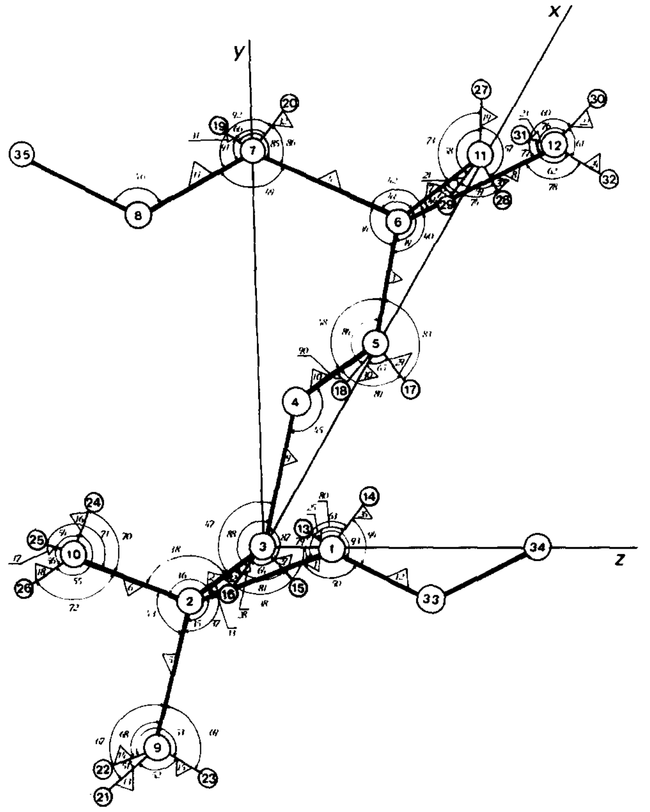

Figure 2 Internal coordinate definitions of poly(3,3-dimethyloxetane) in conformation III

Table 4 Force constants and internal coordinates involved for modification II of poly(3,3-dimethyloxetane)

Force-constant symbol	Internal coordinate[a]	Force-constant value[b]
K_R	1,...,4[c]	4.51
$K_{R'}$	5,...,8	4.61
K_X	9,...,12	4.071*
K_r	13,...,24	4.698
K_d	25,...,32	4.545
H_ω	33, 34	0.95*
H_{ω_1}	35,...,42	0.982*
H_{ω_2}	43, 44	1.097*
H_θ	45, 46	1.527*
H_χ	47,...,50	1.254*
H_α	51,...,62	0.533
H_δ	63,...,66	0.53*
H_β	67,...,78	0.666*
H_γ	79,...,86	0.689*
H_ϕ	87,...,94	0.665*
τ(CC)	95,...,102	0.023
τ(CO)	103,...,105	0.033*
F_R	1–2 1–5 1–6 2–5 2–6 5–6 3–4 3–7 3–8 4–7 4–8 7–8	0.083
F_{RX}	2–9 3–10 4–11 1–12	0.15*
F_X	9–10 12–11′	0.288
$F_{R\beta}$	5–67 5–68 5–69 6–70 6–71 6–72 7–73 7–74 7–75 8–76 8–77 8–78 1–79 1–80 2–81 2–82 3–83 3–84 4–85 4–86	0.174
$F_{R\phi'}$	2–87 2–88 3–89 3–90 4–91 4–92 1–93 1–94	−0.097
$F_{R\omega}$	1–33 2–33 3–34 4–34 1–35 1–36 2–37 2–38 5–35 5–37 6–36 6–38 3–39 3–40 4–41 4–42 7–39 7–41 8–40 8–42 5–43 6–43 7–44 8–44	0.303
$F_{R\chi}$	2–47 3–48 4–49 1–50	0.434
$F_{\chi\theta}$	9–45 10–45 11–46 12–46′	0.483
$F_{X\chi}$	9–47 10–48 11–49 12–50	0.51*
$F_{\chi\phi}$	9–87 9–88 10–89 10–90 11–91 11–92 12–93 12–94	0.27*
$F_{X\gamma'}$	9–81 9–82 10–83 10–84 11–85 11–86 12–79 12–80	−0.095*
F_r	13–14 13–15 14–15 16–17 16–18 17–18 19–20 19–21 20–21 22–23 22–24 23–24	0.032
F_d	25–26 27–28 29–30 31–32	0.019
F_β	67–68 67–69 68–69 70–71 70–72 71–72 73–74 73–75 74–75 76–77 76–78 77–78	−0.035
F_γ	79–80 81–82 83–84 85–86	−0.019
$F'_{\gamma\phi}$	81–87 82–88 83–89 84–90 85–91 86–92 79–93 80–94	0.02*
$F_{\gamma\chi}$	81–47 82–47 87–47 88–47 89–48 90–48 83–48 84–48 85–49 86–49 91–49 92–49 93–50 94–50 79–50 80–50	−0.022*
$f^t_{\beta\omega}$	79–36 80–33 81–38 82–37 67–35 68–37 69–43 70–36 71–43 72–38 83–40 84–34 85–42 86–41 73–39 74–44 75–41 76–40 77–42 78–44	0.08
$f^g_{\beta\omega}$	87–45 88–45 89–45 90–45 79–33 79–35 80–35 80–36 81–33 81–37 82–33 82–36 67–37 67–43 68–35 68–43 69–35 69–37 70–38 70–43 71–36 71–38 72–36 72–43 83–34 83–39 84–39 84–40 85–34 85–41 86–34 86–42 73–41 73–44 74–39 74–41 75–39 75–44 76–42 76–44 77–40 77–44 78–40 78–42 91–46 92–46 93–46′ 94–46′	−0.064
F_ω	33–35 33–36 33–37 33–38 35–36 35–37 35–43 37–38 37–43 36–38 36–43 38–43 34–39 34–40 34–41 34–42 39–40 39–41 39–44 40–42 40–44 41–42 41–44 42–44	−0.041
$f^t_{\omega\chi}$	33–47 39–48 34–49 35–50	0.134
$f^g_{\omega\chi}$	37–47 38–47 34–48 40–48 41–49 42–49 33–50 36–50	−0.01
$f^t_{\chi\theta}$	45–47 45–48 46–49 46′–50	−0.118
F_ϕ	87–88 89–90 91–92 93–94	−0.02

$F_{R\beta}=F_{R\gamma}$; $F_{\gamma\chi}=F_{\phi\chi}$; $f^t_{\beta\omega}=f^t_{\gamma\omega}$; $f^g_{\beta\omega}=f^g_{\gamma\omega}=f^g_{\gamma\theta}$

[a] See *Figures 1* and *2*

[b] Units of force constants are stretch (mdyn Å^{-1}), angle deformation and torsion (mdyn Å rad^{-1}) and angle stretch (mdyn Å)

[c] A,...,B means from A to B

Table 5 Force constants and internal coordinates involved for modification III of poly(3,3-dimethyloxetane). The rest of the internal coordinates are the same as those in modification II

Force-constant symbol	Internal coordinate[a]	Force-constant value[b]
$f^t_{\beta\omega}$	79–33 80–35 81–38 82–33 83–34 84–40 85–41 86–34 67–37 68–35 69–43 70–43 71–36 72–38 73–39 74–41 75–44 76–40 77–44 78–42	0.08
$f^g_{\beta\omega}$	79–35 79–36 80–33 80–36 81–33 81–37 82–37 82–38 87–45 88–45 89–45 90–45 83–39 83–40 84–34 84–39 85–34 85–42 86–41 86–42 77–35 77–43 68–37 68–43 69–35 69–37 70–36 70–38 71–38 71–43 72–36 72–43 73–41 73–44 74–39 74–44 75–41 76–42 76–44 77–40 77–42 78–40 78–44 91–46 92–46 94–46′ 93–46′ 75–39	−0.064
$f^t_{\omega\chi}$	37–47 39–48 42–49 36–50	0.134
$f^g_{\omega\chi}$	33–47 38–47 34–48 40–48 34–49 41–49 33–50 35–50	−0.01
$f^t_{\chi\theta}$	45–47 45–48 46–49 46–50	−0.118

[a] See *Figure 2*

[b] Units of force constants as in *Table 4*

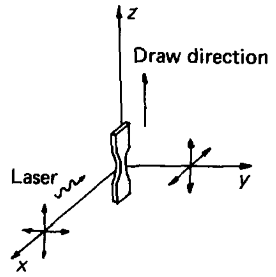

Figure 3 Raman scattering geometry for the drawn samples

Table 6 Symmetry analysis of the crystalline variation II of poly(3,3-dimethyloxetane)

		A′ (A_g)	A″ (B_g)
$x(zz)y$	α'^2_{zz}	α'^2_{zz}	0
$x(yz)y$	$\alpha'^2_{xz}+\alpha'^2_{yz}$	α'^2_{yz}	α'^2_{xz}
$x(zx)y$	$\alpha'^2_{xz}+\alpha'^2_{yz}$	α'^2_{yz}	α'^2_{xz}
$x(yx)y$	α'^2_{xx}, α'^2_{yy}, α'^2_{xy}	α'^2_{xx}, α'^2_{yy}	α'^2_{xy}

Zone 3000–2800 cm^{-1}

The wavenumbers corresponding to the C–H stretching vibrations for the two conformations are observed at 2967 and 2917 cm^{-1} for the CH_3 group and 2870 and 2860 cm^{-1} for the CH_2 group, showing no relation with the conformational state, similarly to other polymers that contain these branched groups[23–27].

Zone 1500–1350 cm^{-1}

The observed frequencies between 1490 and 1450 cm^{-1} can be predominantly assigned to CH_2 and CH_3 bending. The vibrational motions of the conformers are characterized in this region by the difference of the Raman intensities between the bands situated at 1475 and 1485 cm^{-1}, while the other bands (1460 and 1452 cm^{-1}) appear to be independent of the two crystalline modifications and the molten state.

The corresponding symmetrical CH_3 bending vibration (umbrella), which causes a very characteristic band at about 1375 cm^{-1} in polymers containing methyl

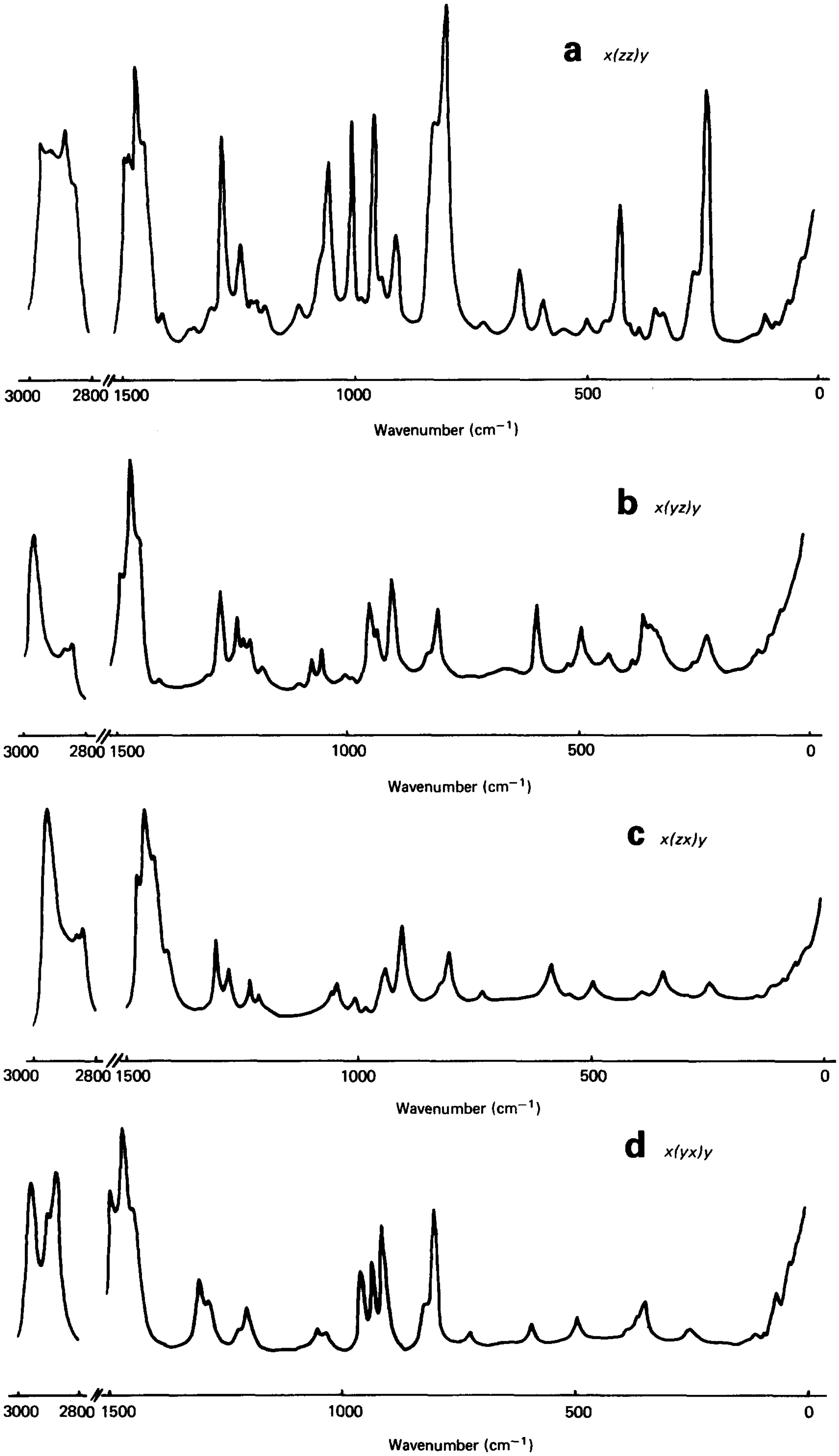

Figure 4 Polarized Raman spectra of PDMO in modification II

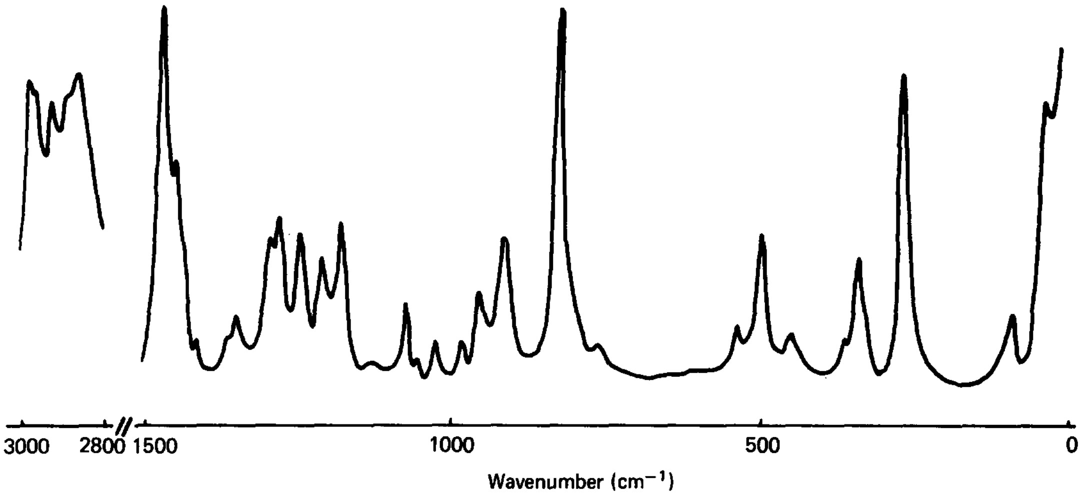

Figure 5 Raman spectrum of PDMO in conformation III

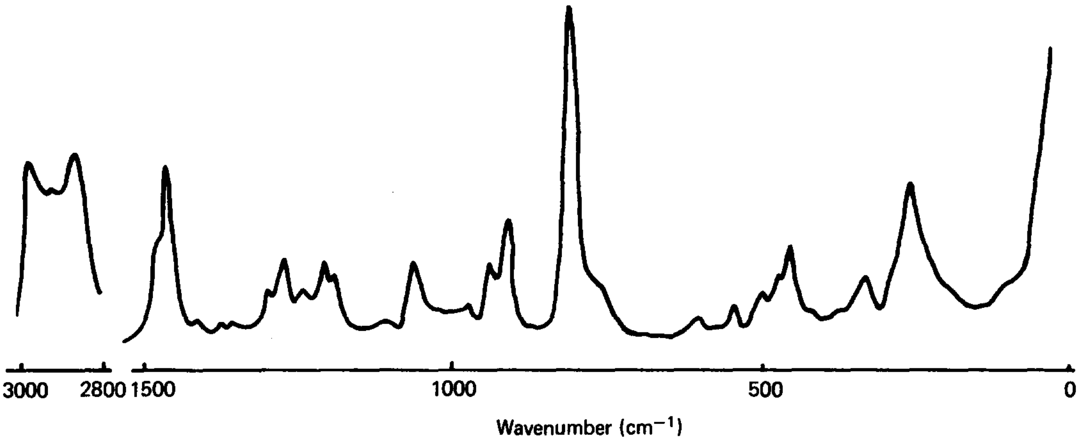

Figure 6 Raman spectrum of molten PDMO

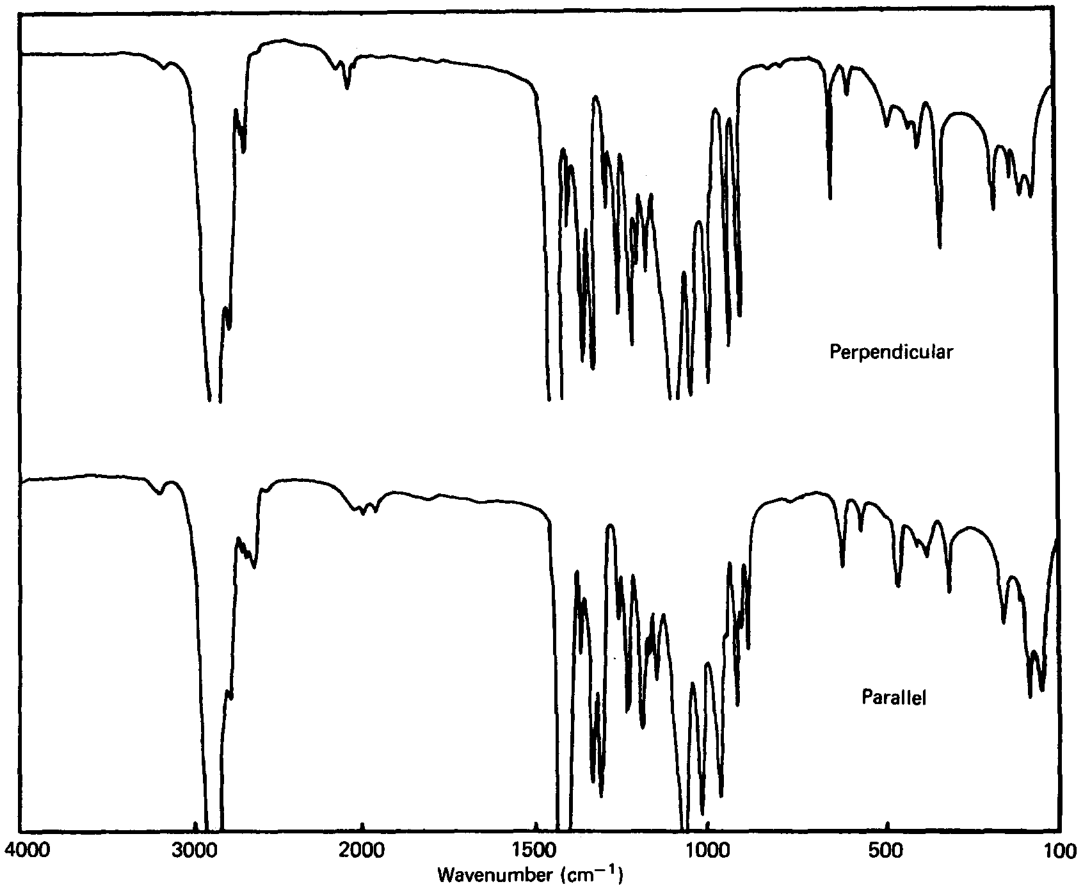

Figure 7 Polarized infra-red spectra of PDMO in conformation II

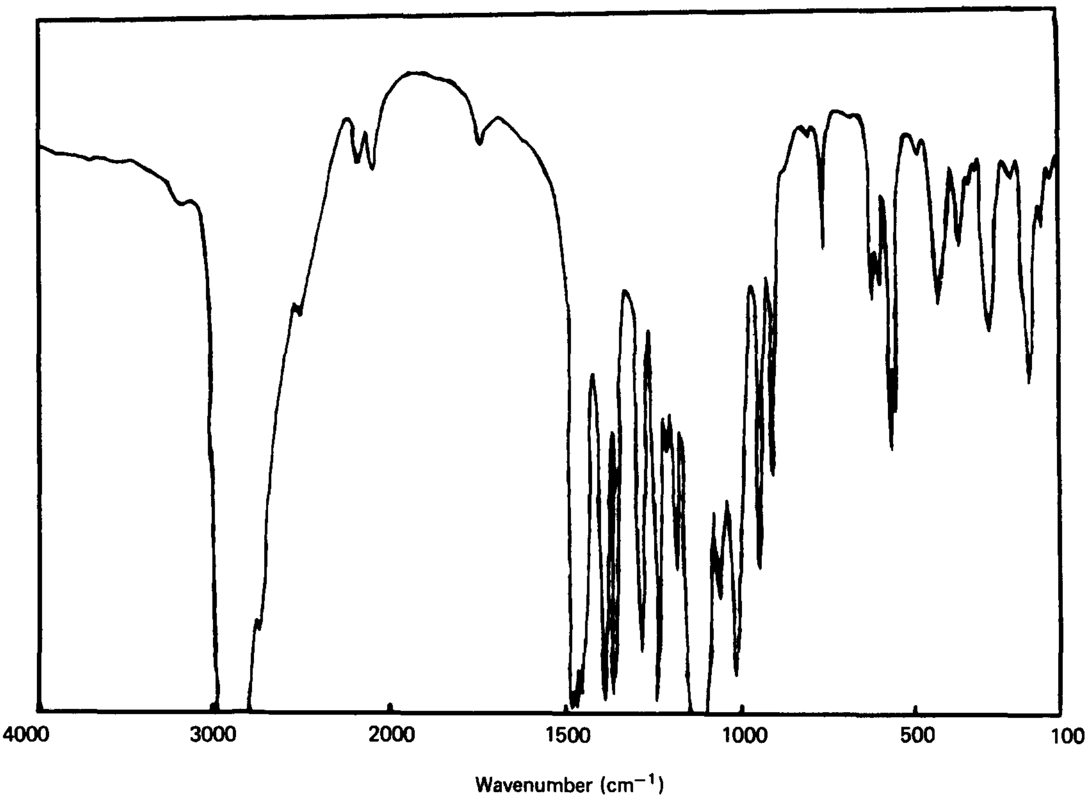

Figure 8 Infra-red spectrum of PDMO in conformation III

Table 7 Observed and calculated frequencies and approximate potential energy distribution for modification II of poly(3,3-dimethyloxetane). Contributions less than 10% are ignored

Calc. freq. A′	Obs. freq.		Assignment and potential energy distribution	Type of vibration
	I.r.	Raman		
2967		2968	100% K_r	$\nu_a(CH_3)$
2965			100% K_r	
2965			100% K_r	
2963			100% K_r	
2919		2917	100% K_d	$\nu_a(CH_2)$
2917			100% K_d	
2877		2870	98% K_r	$\nu_s(CH_3)$
2877			98% K_r	
2859		2860	99% K_d	$\nu_s(CH_2)$
2857			99% K_d	
1480	1480	1478	48% H_α, 19% H_δ, 14% H_β	$\delta(CH_3)$, $\delta(CH_2)$
1474			55% H_α, 13% H_δ, 14% H_β	
1468	1468	1468	69% H_α, 13% H_β	
1457			30% H_α, 52% H_δ	
1456	1460		56% H^α, 30% H_δ	
1456			64% H_α, 23% H_δ	
1411	1420	1423	29% $K_{R'}$, 36% H_α, 31% H_β, −10% $F_{R\beta}$	$U(CH_3)$
1401	1388		17% $K_{R'}$, 44% H_α, 46% H_β	
1371	1370		23% H_α, 25% H_β, 21% H_γ, 15% H_ϕ	$w(CH_2)$, $U(CH_3)$, $t(CH_2)$
1367	1360		15% K_R, 23% H_α, 19% H_β, 19% H_γ	
1367			23% H_α, 21% H_β, 20% H_γ	
1292	1275	1275	21% K_R, 26% H_γ, 30% H_ϕ	$w(CH_2)$, $w(CH_3)$, $t(CH_2)$, $t(CH_3)$
1249	1239	1238	43% H_γ, 45% H_ϕ	
1187	1190	1193	36% H_γ, 43% H_ϕ	
1162	1110	1110	15% $K_{R'}$, 10% H_β, 15% H_γ, 55% H_ϕ	
1054	1060	1059	71% H_β	$t(CH_3)$
1012			17% K_R, 45% H_β	$r(CH_2)$, $r(CH_3)$, $t(CH_2)$, $t(CH_3)$
1004	1003	1003	58% K_X, 24% H_β	$\nu_a(CO)$
982	988	980	17% K_X, 50% H_β	$t(CH_3)$, $r(CH_3)$, $\nu(CO)$
954	947	946	45% K_X, 15% H_ϕ	$t(CH_2)$, $r(CH_2)$, $\delta(COC)$
924	935	936	11% K_X, 11% H_β, 34% H_γ, 25% H_ϕ	$\delta(COC)$
904	910	912	19% $K_{R'}$, 31% H_γ, 27% H_ϕ	$\nu_s(CO)$
876			22% K_R, 23% H_χ, 26% H_γ, 18% H_ϕ	$\nu(CO)$, $r(CH_2)$
798		804	17% K_R, 47% K_R, 19% H_θ	Breathing in phase

Table 7 *continued*

Calc. freq. A′	Obs. freq. I.r.	Obs. freq. Raman	Assignment and potential energy distribution	Type of vibration
632	630	630	12% K_R, 11% H_{ω_1}, 44% H_χ	Skeletal modes
413	424	435	16% H_{ω_1}, 44% H_{ω_2}, 15% H_θ, 12% H_β	
387	377	378	70% H_{ω_1}, 11% H_θ	
341		350	68% H_{ω_1}, 14% H_{ω_2}	
327	325		65% H_{ω_1}, 10% H_θ	
228	236	237	17% K_R, 26% H_{ω_1}, 22% H_θ, 10% H_χ	
133		139	25% H_ω, 15% H_{ω_1}, 26% H_χ, 21% τ(CC)	
112		110	96% τ(CC)	
107			89% τ(CC)	
88		90	16% H_{ω_1}, 41% H_χ, 14% τ(CC), 12% τ(CO)	
75		70	45% τ(CC), 48% τ(CO)	
33			29% τ(CC), 58% τ(CO)	

Calc. freq. A″	Obs. freq. I.r.	Obs. freq. Raman	Assignment and potential energy distribution	Type of vibration
2967		2968	100% K_r	$\nu_a(CH_3)$
2965			100% K_r	
2965			100% K_r	
2963			100% K_r	
2919		2917	100% K_d	$\nu_a(CH_2)$
2917			100% K_d	
2877		2870	98% K_r	$\nu_s(CH_3)$
2877			98% K_r	
2859		2860	99% K_d	$\nu_s(CH_2)$
2857			99% K_d	
1484	1484	1484	13% K_R, 41% H_α, 20% H_δ, 14% H_β, 11% H_γ	$\delta(CH_3)$, $\delta(CH_2)$
1473	1468	1468	60% H_α, 11% H_δ, 14% H_β	
1468			68% H_α, 12% H_β	
1458	1460	1460	21% H_α, 60% H_δ, 11% H_γ	
1456			80% H_α	
1455			46% H_α, 39% H_δ	
1410	1420	1423	29% $K_{R'}$, 36% H_α, 31% H_β, −10% $F_{R\beta}$	$U(CH_3)$
1401	1385		17% $K_{R'}$, 43% H_α, 46% H_β	
1376	1370		15% K_R, 22% H_α, 18% H_β, 15% H_γ, 22% H_ϕ	$w(CH_2)$, $U(CH_3)$, $t(CH_2)$
1354	1360		20% K_R, 17% H_α, 13% H_β, 17% H_γ, 17% H_ϕ	
1350			26% K_R, 17% H_α, 12% H_β, 15% H_γ, 18% H_ϕ	
1286	1305	1306	34% H_γ, 34% H_ϕ	$w(CH_2)$, $w(CH_3)$, $t(CH_2)$, $t(CH_3)$
1245	1239	1238	15% K_R, 40% H_γ, 46% H_ϕ	
1203	1217	1215	30% H_γ, 50% H_ϕ	
1143	1110		14% $K_{R'}$, 13% H_β, 19% H_γ, 47% H_ϕ	
1053	1060	1059	73% H_β	$t(CH_3)$
1023			12% K_R, 24% K_X, 37% H_β	$r(CH_2)$, $r(CH_3)$, $t(CH_2)$, $t(CH_3)$
996	1003	1003	46% K_X, 26% H_β	$\nu_a(CO)$
982	988	980	21% K_R, 25% K_X, 39% H_β	$w(CH_3)$, $t(CH_3)$, $\nu(CO)$
978			13% $K_{R'}$, 32% K_X, 49% H_β, 12% H_ϕ	
923	935	936	13% K_R, 32% K_X, 11% H_χ, 27% H_β, 12% H_γ	$r(CH_2)$, $\nu_s(CO)$
908	910	912	15% K_R, 14% $K_{R'}$, 46% K_X, 12% H_θ, 10% H_χ, 17% H_β, −11% $F_{X\theta}$	$\nu_s(CO)$
879			21% K_R, 23% H_χ, 26% H_γ, 18% H_ϕ	
737		730	34% K_R, 41% $K_{R'}$, 13% H_χ	Breathing out of phase
574	575	581	11% K_R, 27% H_{ω_1}, 19% H_θ, 22% H_χ	Skeletal modes
477	493	495	25% H_{ω_1}, 28% H_χ	
382	377	378	21% H_ω, 50% H_{ω_2}, 10% H_β	
350		350	55% H_{ω_1}, 17% H_θ	
321	325		64% H_{ω_1}, 15% H_θ	
277	252		15% H_ω, 44% H_{ω_1}, 14% H_χ	
204	236	237	64% H_{ω_1}, 21% H_χ	
112		110	98% τ(CC)	
111			99% τ(CC)	
84		90	19% H_χ, 41% τ(CC), 22% τ(CO)	
57		54	12% H_ω, 23% H_χ, 19% τ(CC), 34% τ(CO)	
46		46	63% τ(CC), 27% τ(CO)	

groups, appears shifted in our compound to frequencies of 1388 and 1420 cm^{-1} possibly due to the interaction between the two methyl groups situated on the same bond (9–10 or 11–12 of *Figures 1* and *2*). According to the results of normal-coordinate calculations, the lower-frequency vibration corresponds to the in-phase motion and the higher-frequency one to the out-of-phase movement. Finally, note that the position of these bands is not significantly affected by conformational changes.

Zone 1375–800 cm^{-1}

Assignment of the movements corresponding to the

Table 8 Observed and calculated frequencies and approximate potential energy distribution for modification III of poly(3,3-dimethyloxetane). Contributions less than 10% are ignored

Calc. freq. A	Obs. freq.		Assignment and potential energy distribution	Type of vibration
	I.r.	Raman		
2967		2968	100% K_r	$\nu_a(CH_3)$
2965			100% K_r	
2921		2917	100% K_d	$\nu_a(CH_2)$
2876		2870	98% K_r	$\nu_s(CH_3)$
2858		2864	99% K_d	$\nu_s(CH_2)$
1480		1485	10% K_R, 50% H_α, 14% H_β	$\delta(CH_3)$, $\delta(CH_2)$
1479		1475	44% H_α, 20% H_δ, 13% H_β, 11% H_γ	
1457		1460	48% H_α, 37% H_δ	
1401			16% $K_{R'}$, 44% H_α, 47% H_β	$U(CH_3)$
1374		1360	17% K_R, 21% H_α, 16% H_β, 18% H_γ, 18% H_ϕ	$w(CH_3)$, $U(CH_3)$, $t(CH_2)$
1307		1300	39% H_γ, 42% H_ϕ	$w(CH_2)$, $w(CH_3)$, $t(CH_2)$, $t(CH_3)$
1169			16% H_β, 31% H_γ, 38% H_ϕ	
1057		1067	69% H_β	$t(CH_3)$
1016		1006	14% K_X, 35% H_β, 18% H_ϕ	$r(CH_2)$, $\delta(COC)$, $\nu(CO)$
935		948	53% K_X, 12% H_β, 12% H_γ, 17% H_ϕ, −10% $F_{R\theta}$, −10% $F_{X\theta}$	$\nu_s(CO)$
914			24% K_R, 15% H_θ, 21% H_γ, 16% H_ϕ	$\nu(CC)$, $r(CH_2)$, $t(CH_3)$
826		822	12% K_R, 47% $K_{R'}$	Breathing in phase
505		490	14% H_ω, 35%, H_{ω_2}, 10% H_β	Skeletal modes
325		330	58% H_{ω_1}, 15% H_{ω_2}	
318			35% H_ω, 34% H_{ω_1}, 13% H_θ	
235		268	12% K_R, 21% H_{ω_1}, 19% H_{ω_2}, 13% H_θ	
113			95% τ(CC)	
93		99	12% H_{ω_1}, 18% H_θ, 41% H_χ, 13% τ(CC), 15% τ(CO)	

Calc. freq. B_1	Obs. freq.		Assignment and potential energy distribution	Type of vibration
	I.r.	Raman		
2965		2968	100% K_r	$\nu_a(CH_3)$
2963		2962	100% K_r	
2918		2917	100% K_d	$\nu_a(CH_2)$
2876		2870	98% K_r	$\nu_s(CH_3)$
2856		2864	99% K_d	$\nu_s(CH_2)$
1477	1485	1475	57% H_α, 12% H_δ, 15% H_β	$\delta(CH_3)$, $\delta(CH_2)$
1469			59% H_α, 14% H_δ, 12% H_β	
1454	1453	1452	33% H_α. 49%, H_δ, 11% H_γ	
1405	1420	1420	26% H_R, 38% H_α	$U(CH_3)$
1361		1360	15% K_R, 20% H_α, 17% H_β, 21% H_γ	$w(CH_3)$, $U(CH_3)$, $t(CH_2)$
1354	1353		14% K_R, 19% H_α, 15% H_β, 15% H_γ, 11% H_ϕ	
1231	1239		20% K_R, 36% H_γ, 48% H_ϕ	$w(CH_2)$, $w(CH_3)$, $t(CH_2)$, $t(CH_3)$
1174			13% $K_{R'}$, 11% H_β, 17% H_γ, 51% H_ϕ	
1021	1017		53% K_X, 27% H_β	$\nu_a(CO)$
978		972	14% $K_{R'}$, 59% H_β	$r(CH_2)$, $\nu(CC)$
923	948	914	22% K_X, 21% H_β, 22% H_γ, 19% H_ϕ	$\nu(CO)$, $r(CH_2)$
890			32% K_R, 15%, K_X, 11% H_β, 21% H_γ, 10% H_ϕ	$\nu(CC)$, $t(CH_3)$, $r(CH_2)$
571	564		11% $K_{R'}$, 20% H_{ω_1}, 40% H_χ	Skeletal modes
366			81% H_{ω_1}, 12% H_β	
213	194		68% H_{ω_1}, 40% H_χ	
112	108		98% τ(CC)	
80			51% τ(CC), 49% τ(CO)	
23			41% τ(CC), 56% τ(CO)	

Calc. freq. B_2	Obs. freq.		Assignment and potential energy distribution	Type of vibration
	I.r.	Raman		
2967		2968	100% K_r	$\nu_a(CH_3)$
2965			100% K_r	
2921		2917	100% K_d	$\nu_a(CH_2)$
2876		2870	98% K_r	$\nu_s(CH_3)$
2857		2864	99% K_d	$\nu_s(CH_2)$
1476	1473	1475	50% H_α, 18% H_δ, 13% H_β	$\delta(CH_3)$, $\delta(CH_2)$
1458		1460	39% H_α, 44% H_δ	
1456	1453	1452	80% H_α, 11% H_δ	
1401	1388		16% $K_{R'}$, 44% H_α, 47% H_β	$U(CH_3)$
1364	1362	1360	15% $K_{R'}$, 21% H_α, 17% H_β, 20% H_γ	$w(CH_3)$, $U(CH_3)$, $t(CH_3)$
1260		1254	52% H_γ, 55% H_ϕ	$w(CH_2)$, $w(CH_3)$, $t(CH_2)$, $t(CH_3)$
1186	1186	1186	16% H_β, 23% H_γ, 46% H_ϕ	
1053	1055	1056	69% H_β	$t(CH_3)$
1023		1017	21% K_X, 27%, H_β, 19% H_ϕ	$\nu_a(CO)$
984			60% K_X, 16% H_β	$\nu(CO)$, $\delta(COC)$, $r(CH_2)$
905	909		24% K_R, 15% H_θ, 21% H_γ, 16% H_ϕ	$\nu(CC)$, $t(CH_3)$, $r(CH_2)$
743	764		48% K_R, 23% $K_{R'}$, 19% H_χ, 11% $F_{R\chi}$	Breathing out of phase

Table 8 *continued*

Calc. freq. B_2	Obs. freq.		Assignment and potential energy distribution	Type of vibration
	I.r.	Raman		
576	575		13% $K_{\mathrm{R'}}$, 10% H_{ω}, 38% H_{χ}	Skeletal modes
358	354	348	25% H_{ω_1}, 65% H_{ω_2}, 15% H_{β}	
316	316		31% H_{ω}, 50% H_{ω_1}, 10% H_{γ}	
162	153		25% H_{ω}, 40% H_{ω_1}, 35% H_{χ}	
110	108	99	97% τ(CC)	
58		48	92% τ(CC)	

Calc. freq. B_3	Obs. freq.		Assignment and potential energy distribution	Type of vibration
	I.r.	Raman		
2965		2968	100% K_{r}	$\nu_a(CH_3)$
2963		2962	100% K_{r}	
2918		2917	100% K_{d}	$\nu_a(CH_2)$
2876		2870	98% K_{r}	$\nu_s(CH_3)$
2856		2864	99% K_{d}	$\nu_s(CH_2)$
1469	1473	1475	62% H_{α}, 12% H_{δ}, 12% H_{β}	$\delta(CH_3)$, $\delta(CH_2)$
1458		1460	43% H_{α}, 41% H_{δ}	
1456	1453	1452	78% H_{α}, 12% H_{δ}	
1404	1420	1420	25% $K_{\mathrm{R'}}$, 38% H_{α}, 40% H_{β}, −11% $R_{\mathrm{R}\beta}$	$U(CH_3)$
1372	1362	1360	17% K_{R}, 21% H_{α}, 16% H_{β}, 18% H_{γ}, 18% H_{ϕ}	$w(CH_3)$, $U(CH_3)$, $t(CH_2)$
1353	1353		15% K_{R}, 18% H_{α}, 14% H_{β}, 17% H_{γ}, 12% H_{ϕ}	
1287	1281		13% K_{R}, 15% $K_{\mathrm{R'}}$, 24% H_{γ}, 30% H_{ϕ}	$w(CH_2)$, $w(CH_3)$, $t(CH_2)$, $t(CH_3)$
1157	1130		12% H_{β}, 25% H_{γ}, 46% H_{ϕ}	
996		1002	23% K_{R}, 15% K_{X}, 43% H_{β}	$w(CH_2)$, $r(CH_3)$, ν(CO)
982		972	14% $K_{\mathrm{R'}}$, 59% H_{β}	$r(CH_2)$, δ(COC)
925	948		54% K_{X}, 14% H_{θ}, 15% H_{χ}, 14% H_{β}, −15% $F_{\mathrm{R}\theta}$, −13% $F_{\mathrm{X}\chi}$	ν_s(CO)
885	873		14% $K_{\mathrm{R'}}$, 36% H_{γ}, 35% H_{ϕ}	$r(CH_2)$, δ(COC)
458	442	440	43% H_{ω_1}, 35% H_{θ}, 11% H_{β}, 10% H_{γ}, −11% $f_{\beta\omega}$	Skeletal modes
398	385		14% K_{X}, 58% H_{ω_1}, 19% H_{θ}	
230	261		45% H_{ω_1}, 12% H_{θ}	
115	108		90% τ(CC)	
86			23% H_{ω_1}, 20% H_{θ}, 50% H_{χ}	
55		48	57% τ(CC), 24% τ(CO)	

frequencies observed in this wavenumber region cannot easily be realized in this polymer. A description in terms of rocking, twisting and wagging modes of the CH_2 and CH_3 groups is only possible for a few frequencies, classified by the influence of the main movements. The majority of these modes agree with well established group frequencies. Thus, the high-frequency region is contributed to principally by CH_2 wagging with the presence of CH_3 symmetric bending and wag-like motions of the methyl groups. It is suggested from normal-coordinate analysis that the band at 1059 cm^{-1} may be assigned to a CH_2 twisting and twist-like motions of the methyl groups.

The most important contribution in the low-frequency region involves a complex combination of C–C and C–O stretching and CH_2 rocking with some contribution from angular chain deformation around the oxygen bond.

The results obtained by other authors from normal-coordinate calculations on oligomers of the linear polyether type[34–36] indicated the possibility of studying the conformational structure of linear polyethers through analysis of the vibrational wavenumbers in the 800–1000 cm^{-1} region, corresponding to C–O stretching and CH_2 rocking. The vibrational spectra in this region are very sensitive to the conformation of the bond following the C–O bond (related to the internal coordinate 3 in *Figure 2*). In our compound the conformational changes between the two crystalline modifications are situated on this bond. However, the vibrational spectra of PDMO in this region are more complex than those of linear polyethers. In this sense, the variations in intensity and wavenumbers observed between both conformers are too complicated to be used in the study of conformational characterization of PDMO.

Otherwise, the normal-coordinate treatment describes an isolated band at 798 cm^{-1} for variation II (A′ mode) and 826 cm^{-1} for variation III (A mode) assigned to the movement described in *Figure 9* (breathing mode). As we can see, the movement on the side groups makes an important contribution to this vibration, which characterizes branched polyethers. The Raman spectra present two very strong lines at 804 cm^{-1} (form II) and 822 cm^{-1} (form III) with a low contribution from the amorphous phase (band at 815 cm^{-1}). The polarization ratios of this band for variation II is the highest of the spectrum, therefore showing a strong intermolecular coupling. According to this, it can be concluded that these characteristic bands of PDMO are a good key to identifying the conformational variations, since they present the following characteristic: isolated and intense band from a pure and characteristic mode.

These last bands were used to study the evolution of the conformers present in the sample with change in external variables (annealing temperature, pressure, stretching, etc.). A deeper discussion about this characterization has already been presented[4,7,10].

Zone below 700 cm^{-1}

The normal modes occurring below 700 cm^{-1} arise from the skeletal motions and, therefore, great differences

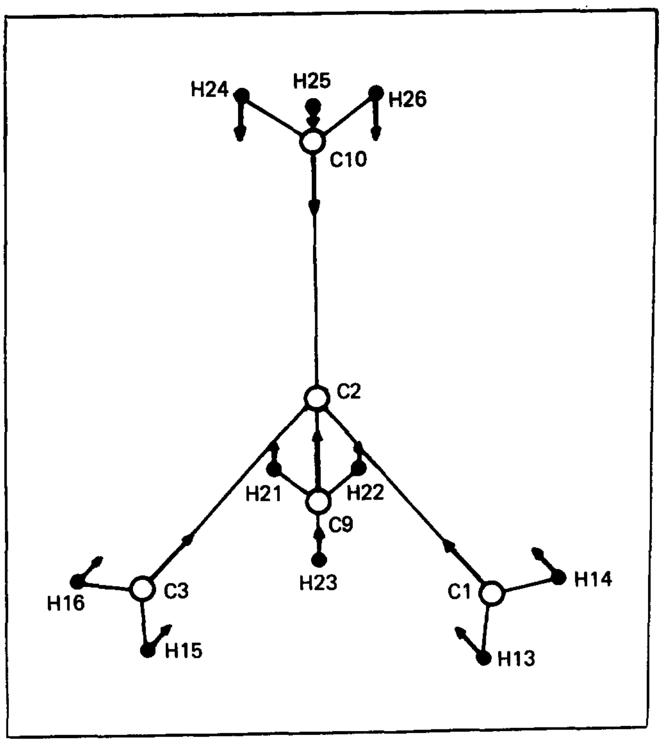

Figure 9 Normal mode corresponding to the frequencies of 804 cm^{-1} (modification II) and 822 cm^{-1} (modification III)

in the vibrational spectra of the two conformers were observed. However, a comparison of the spectra in the torsional modes region (about 110 cm^{-1}) reveals only minor differences between the results of the two crystalline conformations.

The vibrational assignment obtained for the crystalline modification III is very similar to the other modification. The most important influence of chain conformation III is reflected by the significant changes observed in the wagging and twisting zone, as well as in those previously discussed.

CONCLUSIONS

Normal-coordinate calculations have been performed on the molecular chain of two crystalline conformations of poly(3,3-dimethyloxetane). The agreement between the observed and calculated frequencies in both conformers are excellent and we have been able satisfactorily to assign the normal modes for both crystalline modifications with good confidence. The band corresponding to the breathing motion, characteristic of other branched polyethers, has been determined as the region most sensitive to the molecular conformation.

The refined VFF obtained for the two chain conformations of this polymer is presented as the first result for the polyether series with various branch lengths. We intend to expand this vibrational study to other elements transferring the force field, and finally an available conformational characterization of branched polyethers could be presented.

On the other hand, the results presented here are focused mainly on detecting the different conformations of the polymer. In this way analysis of the chain conformations by Raman spectroscopy has allowed us to follow the evolution of the crystal modifications after submitting the sample to thermal, stretching and pressure processes. In previous papers[4,5,10] we have shown changes in conformation of PDMO with the temperature of crystallization and annealing, time of crystallization and pressure on the basis of the vibrational assignment presented here.

A similar vibrational study for poly(3,3-diethyloxetane), to be published, has also allowed us to realize a conformational characterization and has been used to evaluate the behaviour of conformers of the compound.

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