

CONFORMATIONAL STRUCTURE OF POLY[2-(DIMETHYLAMINO)ETHYL METHACRYLATE], 2-(DIMETHYLAMINO)ETHYL PIVALATE AND OF THEIR QUATERNARY IODIDES.\*  
VIBRATIONAL AND NMR SPECTRA

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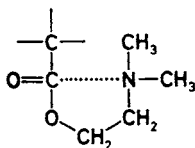
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Raman, infrared, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2-(dimethylamino)ethyl pivalate, 2-(pivaloyloxy)ethyltrimethylammonium iodide, poly[2-(dimethylamino)ethyl methacrylate] and of its quaternary iodide were measured. Spectral analysis revealed that in crystalline 2-(dimethylamino)ethyl pivalate and in its quaternary salt, the 2-(dimethylamino)ethyl group exists in the *g* conformational state. In the liquid state, these compounds also contain a smaller amount of the *t* conformational structure of the 2-(dimethylamino)ethyl group. In poly[2-(dimethylamino)ethyl methacrylate] and in its quaternary iodide in solution, the population of the *g* and *t* conformational structures are similar to those found in 2-(dimethylamino)ethyl pivalate and in its quaternary iodide.

Poly[2-(dimethylamino)ethyl methacrylate] (pDMAEM),  $[\text{CH}_2-\text{C}(\text{CH}_3)\text{COOCH}_2 \cdot \text{CH}_2\text{N}(\text{CH}_3)_2]_n$ , its simplest low-molecular model 2-(dimethylamino)ethyl pivalate (DMAEP),  $(\text{CH}_3)_3\text{CCOOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ , and their quaternary iodides, poly[2-(methacryloyloxy)ethyltrimethylammonium iodide] (pMOETMAI),  $[\text{CH}_2\text{C}(\text{CH}_3) \cdot \text{COOCH}_2\text{CH}_2\text{N}^{(+)}(\text{CH}_3)_3 \cdot \text{I}^{(-)}]_n$ , and 2-(pivaloyloxy)ethyltrimethylammonium iodide (POETMAI),  $(\text{CH}_3)_3\text{CCOOCH}_2\text{CH}_2\text{N}^{(+)}(\text{CH}_3)_3 \cdot \text{I}^{(-)}$ , exhibit in some reactions and during dissociation a behaviour which is explained by a cyclic structure of the 2-(dimethylamino)ethyloxycarbonyl group<sup>1,2</sup>.

In order to determine the possibilities of cyclic structure formation in DMAEP,



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pDMAEM and in their iodides, we have attempted to determine by means of vibrational and NMR spectra the conformational structure of the dimethylamino-ethylester group in DMAEP and pDMAEM, and in the 2-(acyloxyethyl)trimethylammonium groups of the quaternary iodides. The present spectral analysis was based on the results obtained in studies of 2-(dimethylamino)ethanol (DMAE),  $(\text{CH}_3)_2 \cdot \text{NCH}_2\text{CH}_2\text{OH}$ , its methyl ether (MDMAEE),  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OCH}_3$ , and of the corresponding quaternary iodides, i.e.  $(\text{CH}_3)_3\text{N}^{(+)}\text{CH}_2\text{CH}_2\text{OH} \cdot \text{I}^{(-)}$  (HETMAI), and  $(\text{CH}_3)_3\text{N}^{(+)}\text{CH}_2\text{CH}_2\text{OCH}_3 \cdot \text{I}^{(-)}$  (MOETMAI) (ref.<sup>3</sup>).

## EXPERIMENTAL

### Compound Synthesis

Poly[(2-dimethylamino)ethyl methacrylate] (pDMAEM) samples were prepared by radical (sample I) and anionic (sample II) solution polymerization<sup>4</sup>; the quaternization of polymers was carried out using methyl iodide as an alkylating agent<sup>2</sup>. 2-(Dimethylamino)ethyl pivalate (DMAEP) was prepared<sup>5</sup> from pivaloyl chloride (Fluka) and 2-(dimethylamino)ethanol (Fluka). 2-(Pivaloyloxy)ethyltrimethylammonium iodide (POETMAI) was prepared by the reaction of 2-(dimethylamino)ethyl methacrylate (86.5 g; 0.5 mol) with methyl iodide (80 g; 0.56 mol) in 400 ml of hexane at ambient temperature and drying.

### Measurements

*Raman spectra* were measured with the spectrometer Coderg LRDH-800 connected on line with the multichannel spectra analyzer TN-11 Tracor Northern. The spectra were excited by the line 514.5 nm of the argon laser CR-3 (Coherent Radiation). The spectra were measured in the 90° arrangement and were accumulated from several scans. The low temperature spectra were measured in cells with an evacuated jacket.

*Infrared spectra* were measured with the spectrometer Perkin-Elmer 621 connected on-line with the multichannel spectra analyzer TN-4000 (Tracor Northern).

*NMR spectra* were measured with the FT NMR spectrometer AM-200 (Bruker). The sample of DMAEP was measured as a 15% solution in  $\text{CDCl}_3$ , the sample of the pDMAEM polymer was also measured in  $\text{CDCl}_3$  solution. As the polymer is insoluble after drying, its solution was prepared as follows: A stock solution of pDMAEM in  $\text{CHCl}_3$  was evaporated to a very viscous state,  $\text{CDCl}_3$  was added and the mixture was once more evaporated. The sample for measurement was obtained by further addition of  $\text{CDCl}_3$ . Hexamethyldisiloxane (HMDS) was added to this sample as internal reference. The solution of pDMAEM in *o*-dichlorobenzene (ODCB) was prepared in a similar way. The samples of MOETMAI and POETMAI were prepared as 20% and 10% solutions in  $\text{D}_2\text{O}$ , respectively, with sodium 4,4-dimethyl-4-sila-1-pentanesulfonate (DSS) added as reference.  $^1\text{H}$  NMR spectra were measured at 200.13 MHz. Spectra of DMAEP were measured at room temperature and at 213 K; spectra of pDMAEM were measured in  $\text{CDCl}_3$  at ambient temperature, and in ODCB in the range 300–413 K. The sample of POETMAI was measured at ambient temperature; the sample of pMOETMAI at ambient temperature and at 374 K.  $^{13}\text{C}$  NMR spectra were measured at 50.32 MHz, both fully coupled, and with broad band  $^1\text{H}$  decoupling. The sample of DMAEP was measured at ambient temperature and at 213 K, the sample of pDMAEM at ambient temperature only.

## RESULTS AND DISCUSSION

## DMAEP and POETMAI

$^1\text{H}$  NMR spectra of DMAEP and POETMAI are shown in Fig. 1a and 2a. In all spectra, the bands of  $\text{CCH}_3$  and  $\text{NCH}_3$  groups appear as singlets, at positions given in Table I. The bands of  $\text{NCH}_2\text{—CH}_2\text{O}$  groups in both compounds have the

TABLE I

$^1\text{H}$  NMR chemical shifts,  $\delta$ , of the studied molecules (ppm from HMDS or DSS)

Compound	N— $\text{CH}_3$	C— $\text{CH}_3$	N— $\text{CH}_2$	O— $\text{CH}_2$
DMAEP <sup>a</sup>	2.22	1.14	2.50	4.11
POETMAI <sup>b</sup>	3.25	1.21	3.80	4.55
pDMAEM <sup>a</sup>	2.23 <sup>d</sup> , 2.22 <sup>c</sup>	0.99 <sup>d</sup> , 0.83 <sup>c</sup>	2.50	4.00
pMOETMAI <sup>b</sup>	3.31	1.11 <sup>d</sup> , 1.04 <sup>c</sup>	3.89	4.56

<sup>a</sup> Solution in  $\text{CDCl}_3$  at ambient temperature,  $\delta$  from HMDS; <sup>b</sup> solution in  $\text{D}_2\text{O}$  at ambient temperature,  $\delta$  from DSS; <sup>c</sup> *syndiotactic* triad; <sup>d</sup> *heterotactic* triad.

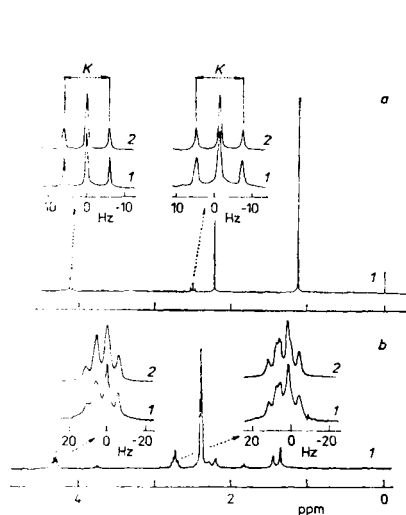


FIG. 1

$^1\text{H}$  NMR spectra of DMAEP in  $\text{CDCl}_3$  at ambient temperature (a) and of pDMAEM (sample I) in ODCB at 413 K (b): 1 experimental, 2 simulated (see text)

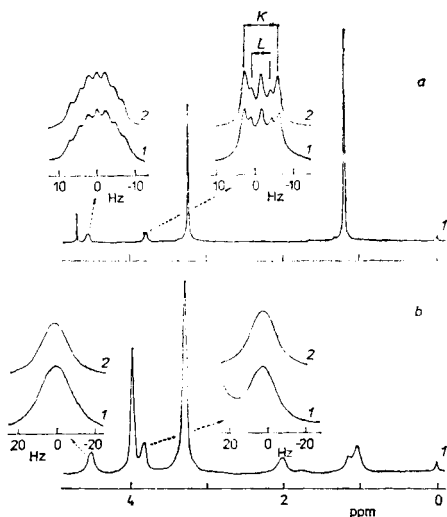


FIG. 2

$^1\text{H}$  NMR spectra of POETMAI in  $\text{D}_2\text{O}$  at ambient temperature (a) and of pMOETMAI in  $\text{D}_2\text{O}$  at 370 K (b): 1 experimental, 2 simulated (see text)

form of AA'XX' multiplets. Similarly as with DMAE and MDMAEE<sup>3</sup>, also in DMAEP the bands of the OCH<sub>2</sub> and CH<sub>2</sub>N groups appear as two triplets, at 4.1 and 2.5 ppm, respectively, in which the spacing of the outer triplet components ( $K = J_{AX} + J_{AX'}$ ) is equal to 11.9 Hz at 297 K and to 11.6 Hz at 213 K. The lack of splitting of the central peak in the triplet indicates  $L \rightarrow 0$ , with  $J_{AX} \doteq J_{AX'}$ . In POETMAI the NCH<sub>2</sub> and OCH<sub>2</sub> bands exhibit a more complicated structure; the band of the OCH<sub>2</sub> group at 4.5 ppm is broadened and split by coupling with the <sup>14</sup>N(+) nucleus<sup>7</sup> (Fig. 2a). The band of the NCH<sub>2</sub> group at 3.8 ppm appears as a well resolved quintet, with the spacing of the outer bands ( $K = J_{AX} + J_{AX'}$ ) equal to 8.9 Hz, and the spacing of the inner triplet,  $|L| = |J_{AX} - J_{AX'}|$ , equal to 5.4 Hz (Fig. 2a). (The band at 4.7 ppm corresponds to HDO in the solvent.) The values  $K$  and  $L$  were used to determine the vicinal proton coupling constants in NCH<sub>2</sub>—CH<sub>2</sub>O groups ( $J_{AX}, J_{AX'}$ ); these values were checked by means of the programme "PANIC" for NMR spectra analysis, included in the equipment of the AM 200 spectrometer. The experimental values obtained by analysis of the NCH<sub>2</sub> band are shown in Table II.

The spectrum of the —NCH<sub>2</sub>—CH<sub>2</sub>O— group in POETMAI was simulated as an AA'XX'Q system, Q being a nucleus of spin 1, with the coupling constants  $J_{QX} = J_{QX'} = 0$ ;  $J_{QA} \neq J_{QA'} \neq 0$ . The simulated spectrum for the values  $J_{AX} = 6.8$  Hz,  $J_{AX'} = 1.8$  Hz and  $J_{QA} = 4.3$  Hz,  $J_{QA'} = 0.7$  Hz is represented by curve 2 in Fig. 2.

If we make the same assumption as with the previously studied molecules DMAE, MDMAEE and the corresponding iodides, namely that only staggered conformers can be formed by rotation about the CH<sub>2</sub>—CH<sub>2</sub> bond (Fig. 3a) and designating these structures as **t**, **g**<sub>1</sub> and **g**<sub>2</sub>, then the following relations are valid<sup>3</sup> (with  $x_{g_1} = x_{g_2} = x_g$  because of symmetry)

$$x_t + 2x_g = 1, \quad (1)$$

$$J_{AX} = x_t J_T + 2x_g J_G, \quad (2)$$

$$J_{AX'} = x_t J_G + x_g (J_G + J_T); \quad (3)$$

$x_t, x_g$  are the populations of the conformers **t** and **g**, and the parameters  $J_T$  and  $J_G$  are the <sup>3</sup> $J_{HH}$  values for the dihedral angles 180° and 60°, respectively, between the bonds carrying the coupled protons.

The equal values of the  $J_{AX}$  and  $J_{AX'}$  coupling constants in DMAEP (Table II) indicate that the  $x_g$  and  $x_t$  populations are approximately equal, similarly as in DMAE and MDMAEE. The mild drop of the  $K$  parameter (spacing of the outer peaks of the NCH<sub>2</sub> triplet) in DMAEP with decreasing temperature indicates some increase in the contents of conformational structures with the **g** form with decreasing temperature.

In the quaternary iodide POETMAI the values of  $J_{AX}$  and  $J_{AX'}$  differ considerably; this indicates that in the solutions of POETMAI one of the conformational structures generated by rotation about the  $OCH_2-CH_2N$  bond strongly predominates. The values of the vicinal coupling parameters  $J_G$  and  $J_T$  calculated from Eqs (1)–(3) and the data in Table II, are  $J_G = 1.7$  and  $J_T = 12.5$  for  $x_t = 0$ ; or  $J_G = 1.7$ ,  $J_T = 7.1$  for  $x_g = 0$ . On arguments similar to those discussed in ref.<sup>3</sup>, the former combination appears as the more realistic, indicating predominant *g* conformational structure of the aminoethyl group in POETMAI, similarly as in the case of HETMAI and MOETMAI.

$^{13}C$  chemical shifts in  $^{13}C\{^1H\}$  spectra of POETMAI are shown in Table III. A part of the fully coupled  $^{13}C$  NMR spectrum of DMAEP is shown in Fig.4. From this spectrum the value of the coupling constant  $^3J(CH_3NCH_2)$  can be measured; this constant depends on the conformational structure generated by rotation about the C—N bond by the relation<sup>3,8,9</sup>  $^3J_{CH} = A \cos^2 \Theta$ , where  $\Theta$  is the dihedral angle

TABLE II  
Proton vicinal coupling constants in the group  $CH_2-CH_2O$

Compound	Temperature K	$J_{AX}$ , Hz	$J_{AX'}$ , Hz
DMAEP	room	5.95	5.95
	213	5.80	5.80
pDMAEM	353	5.85	5.85
	413	5.85	5.85
POETMAI	room	1.75	7.15

TABLE III  
 $^{13}C$  chemical shifts,  $\delta$ , of the studied molecules (ppm from HMDS or DSS)

Compound	( $\alpha$ )C—CH <sub>3</sub>	N—CH <sub>3</sub>	N—CH <sub>2</sub>	O—CH <sub>2</sub>	C=O
DMAEP <sup>a</sup>	25.3	43.9	56.0	60.7	176.3
POETMAI <sup>b</sup>	29.1	57.0	61.2	67.7	182.5
pDMAEM <sup>a</sup>	15.0 <sup>d</sup> , 16.7 <sup>c</sup>	43.8	55.2	61.1	175.5 <sup>d</sup> , 174.5 <sup>c</sup>
pMOETMAI <sup>b</sup>	21.8	56.6	61.7	66.5	180.0 <sup>d</sup> , 179.5 <sup>c</sup>

<sup>a</sup> Solution in  $CDCl_3$ ,  $\delta$  from HMDS; <sup>b</sup> solution in  $D_2O$ ,  $\delta$  from DSS; <sup>c</sup> *syndiotactic* triad; <sup>d</sup> *heterotactic* triad.

between the bonds  $\text{CH}_3\text{—N}$  and  $\text{NC—H}$  and  $\cos^2 \theta$  is averaged over all equivalent positions following from the symmetry of the molecule. In the staggered approximation, rotation about the  $\text{C—N}$  bond in DMAEP and pDMAEM can produce the structures  $g^N$  and  $t^N$  shown in Fig. 3b. By the coupling constants  ${}^3J(\text{CH}_3\text{NCH}_3)$  and  ${}^3J(\text{CH}_3\text{NCH}_2)$ , each component of the  $\text{NCH}_3$  quartet in the  ${}^{13}\text{C}$  NMR spectrum of DMAEP is split into  $4 \times 3$  bands. The shape of the  $\text{NCH}_3$  multiplet was simulated by the programme PANIC as an  $\text{AX}_3\text{Y}_3\text{Z}_2$  system. From this simulation, the best values of the  ${}^3J(\text{CH}_3\text{NCH}_3)$  and  ${}^3J(\text{CH}_3\text{NCH}_2)$  coupling constants were found equal to 5.5 and 4.7 Hz. The corresponding simulated spectrum is shown in Fig. 4. The found coupling constants are practically identical with the corresponding values found for DMAE and MDMAEE<sup>3</sup>. This indicates that the population of structures generated by rotation about the  $\text{C—N}$  bond in DMAEP is equal as in DMAE and MDMAEE where detailed considerations of coupling constant values lead to the conclusion that in solutions of these compounds both  $g^N$  and  $t^N$  structures are present, with the population of  $g^N$  higher than that of  $t^N$ .

The Raman spectrum of liquid DMAEP is shown in Fig. 5a. By cooling of a liquid sample in a Raman cell, we have under certain conditions succeeded in measuring the spectrum of this compound in the solid state (Fig. 5b). Comparison of these two spectra reveals that transition from liquid to solid state is accompanied by the disappearance of bands appearing in liquid DMAEP at 772, 986 and 1 036  $\text{cm}^{-1}$ , and to a shift of the  $\text{C=O}$  stretching vibration band from 1 728 to 1 710  $\text{cm}^{-1}$ . This indicates that the spectrum in Fig. 5b corresponds to crystalline DMAEP. We have also followed the intensity changes of DMAEP bands occurring in the temperature

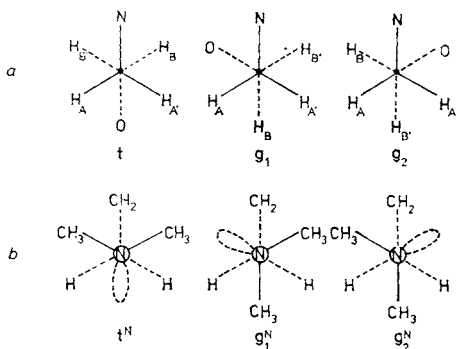


FIG. 3

Schematic representation of the conformers generated by rotation about the bonds  $\text{CH}_2\text{—CH}_2$  (a) and  $\text{C—N}$  (b)

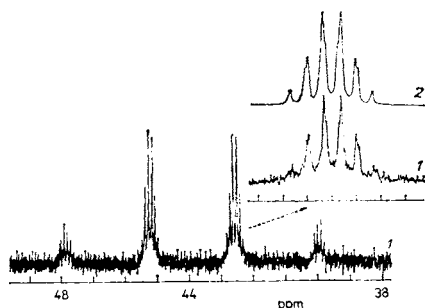


FIG. 4

${}^{13}\text{C}$  NMR spectrum of the  $\text{NCH}_3$  multiplet in POETMAI, with full  ${}^1\text{H}$  coupling, in  $\text{CDCl}_3$  at ambient temperature: 1 experimental, 2 simulated, both curves 10 times expanded

range 300–193 K. In these measurements, three strong bands are observed in the range 700 to 900  $\text{cm}^{-1}$ , at 772, 804 and 844  $\text{cm}^{-1}$ . The strong band at 804  $\text{cm}^{-1}$ , of temperature independent intensity, and unaffected by crystallization, evidently corresponds to the vibration which is characteristic of pivalic acid esters<sup>10</sup>. The bands at 772 and 844  $\text{cm}^{-1}$  appear at practically equal wavenumbers as the bands sensitive to conformational structures generated by rotation about the C—C bond in DMAE and MDMAEE; in the latter two compounds, the band at 772  $\text{cm}^{-1}$  which disappears on crystallization has been assigned to the *t* forms, and the band at 844  $\text{cm}^{-1}$  to the *g* form. In DMAE, MDMAEE and DMAEP at room temperature, the relative intensity of these two bands is approximately equal. With all these compounds, cooling of the liquid samples leads to an intensity decrease of the band at 772  $\text{cm}^{-1}$  and to an intensity increase of the band at 844  $\text{cm}^{-1}$ . Based on these data, and on the results of NMR spectral analysis we assume that also for DMAEP the band at 772  $\text{cm}^{-1}$  corresponds to the *t* form of the 2-(dimethylamino)ethyl group, and the band at 844  $\text{cm}^{-1}$  to the *g* form of this group. For the other bands disappearing during

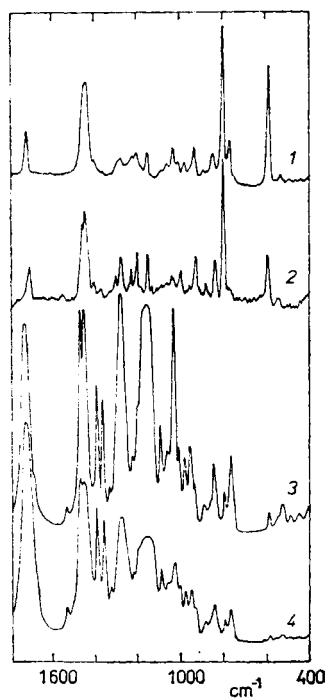


FIG. 5

Raman (1, 2) and infrared (3, 4) spectra of DMAEP; 1, 3 liquid, 2 crystal, 4 glass

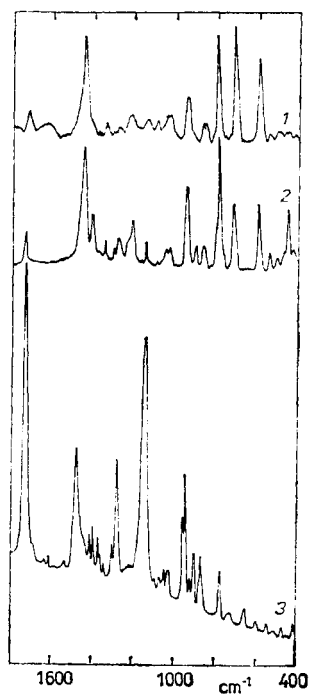


FIG. 6

Raman (1, 2) and infrared (3) spectrum of POETMAI; 1 aqueous solution, 2, 3 crystal

crystallization of DMAEP (986 and  $1\,038\text{ cm}^{-1}$ ) it cannot be decided whether these bands are sensitive to the *t* and *g* conformational structures of the 2-(dimethylamino)ethyl group, or if they are sensitive to conformational structures generated by rotation about other bonds of this molecule.

In the cells for the measurement of infrared spectra, DMAEP could not be crystallized. Therefore the infrared spectra of this compound were only measured in the liquid and in the glassy states (Fig. 5). But for insignificant changes in the wavenumbers, intensities and widths of some bands, the infrared spectra of liquid and solid DMAEP are practically identical. This is evidently connected with the circumstance that practically all bands appearing in the range  $400$  to  $1\,300\text{ cm}^{-1}$  in the infrared spectrum correspond to the pivalate group, and overlap the bands of the 2-(dimethylamino)ethyl group. From the infrared spectra it can be concluded that the conformational structure of the pivalate group does not change with temperature. Band positions in infrared spectra indicate that the conformational structure of the pivalate group in DMAEP is equal as in methyl pivalate for which a structure with *syn* orientation of the  $\text{C}-\text{CH}_3$  and  $\text{O}-\text{CH}_3$  groups with respect to carbonyl has been proposed<sup>10</sup>.

The Raman spectra of POETMAI in aqueous solution and in the crystalline state, and the infrared spectrum of crystalline POETMAI are shown in Fig. 6. From this figure it can be seen that none of the Raman bands of the aqueous solution disappears by crystallization. In the crystalline state some bands exhibit a splitting corresponding to crystal lattice interactions. Similarly as with the Raman spectra of crystalline HETMAI and MOETMAI, also in the spectra of crystalline POETMAI there appear sharp bands at  $450$  and  $1\,400\text{ cm}^{-1}$  characteristic of quaternary (oxyethyl)trimethylammonium iodides. The circumstance that no conformationally sensitive band could be found in the vibrational spectra of POETMAI is in agreement with the results of NMR analysis indicating that in the solutions of this compound only the *g* structure is present.

#### pDMAEM and pMOETMAI

<sup>1</sup>H NMR spectra of pDMAEM and pMOETMAI are shown in Fig. 1b and 2b. The bands of the pDMAEM proton groups are sensitive to the configurational structure of the polymer (Table I). Measurements of two pDMAEM samples prepared by different methods confirmed the effect of stereoregularity on  $-\text{NCH}_3$  and  $\alpha\text{-CH}_3$  signals, and these were assigned to *syndiotactic* and *heterotactic* triads by analogy with poly(methyl methacrylate)<sup>11</sup>, as shown in Table I. Measurements have shown that the sample I (Fig. 1b and 2b) contains 63% *syndiotactic*, 34% *heterotactic* and 3% *isotactic* triads. The stereoregularity of the sample II does not differ substantially from that of the sample I. With pMOETMAI the bands are broader, even when measured at higher temperature, and configurational structure is only



manifested by separated  $\alpha$ -CH<sub>3</sub> bands. (At 4 ppm the spectrum also exhibits a peak of HDO from the solvent.) In pDMAEM, the OCH<sub>2</sub> and NCH<sub>2</sub> bands have the appearance of complicated multiplets (Fig. 1b) Table I. Analysis by the programme PANIC confirmed that these multiplets can be described by overlap of AA'XX' triplets of *syndiotactic* and *heterotactic* triads. The simulated multiplets of —OCH<sub>2</sub>—CH<sub>2</sub>—N protons shown in Fig. 1b were computed with the vicinal coupling constants  $J_{AX} = J_{AX'} = 6.0$  Hz and *syndiotactic* and *heterotactic* triad populations of 63 and 34%, respectively. <sup>1</sup>H NMR spectra of pDMAEM in ODCB were measured in the temperature range 303–413 K. Already at the temperature of 353 K, the OCH<sub>2</sub> and NCH<sub>2</sub> bands were so resolved that the values of the coupling constants  $J_{AX}$  and  $J_{AX'}$  could be measured. The values determined from NCH<sub>2</sub> band analysis are shown in Table II. The coupling constant values are temperature independent and for pDMAEM practically equal to those found in DMAEP, indicating that the forms generated by rotation about the bond OCH<sub>2</sub>—CH<sub>2</sub>N are equally populated in the two compounds, i.e.  $x_g \approx x_t$ .

In pMOETMAI, the OCH<sub>2</sub> and NCH<sub>2</sub> bands are broad and unresolved (Table I) even at higher temperatures (Fig. 2b). We have simulated the expected shape of these bands for AA'XX' multiplets with  $J_{AX} = 1.8$  Hz and  $J_{AX'} = 6.8$  Hz, taken over from the analysis of POETMAI, and with *syndiotactic* and *heterotactic* triad overlap similar to pDMAEM. The simulated curves agree well with the measured spectra (Fig. 2b). This result conforms with the assumption that in pMOETMAI, the predominant form generated by rotation about the OCH<sub>2</sub>—CH<sub>2</sub>N bond is the *g* structure, similarly as in POETMAI.

The chemical shifts in <sup>13</sup>C{<sup>1</sup>H} NMR spectra of pDMAEM and pMOETMAI are shown in Table III. The spectra reflect the configurational structure of the polymer. Fully coupled <sup>13</sup>C NMR spectra of these polymers, with a resolution sufficient for conformational analysis, could not be obtained.

Raman and infrared spectra of pDMAEM and pMOETMAI are shown in Figs 7 and 8. The Raman spectrum of pDMAEM is similar to the Raman spectrum of liquid DMAEP. In the range 900–750 cm<sup>-1</sup>, where Raman spectra of DMAEP exhibit a strong band of the ester group at 804 cm<sup>-1</sup> and the pair of conformationally sensitive bands at 770 and 849 cm<sup>-1</sup> assigned to *t* and *g* conformational structures, pDMAEM also shows three bands at 874, 828 and 778 cm<sup>-1</sup>; of these, the band at 828 cm<sup>-1</sup> is the strongest and evidently corresponds to the ester group. Based on the results of <sup>1</sup>H NMR analysis of pDMAEM we assume that the bands at 874 and 778 cm<sup>-1</sup> correspond to *t* and *g* conformational structures of pDMAEM. The intensity ratio of these two bands is equal to that of the bands at 849 and 770 cm<sup>-1</sup> in DMAEP, in agreement with <sup>1</sup>H NMR results, indicating that the population of *g* and *t* conformational structures in DMAEP is equal to that in pDMAEM. Similarly as with DMAEP, also in the infrared spectrum of pDMAEM (Fig. 7b), the bands of the ester group are the strongest. We have measured the infrared spectra of

pDMAEM films in the temperature range 300–523 K, and of pDMAEM solutions in  $\text{CHCl}_3$  and in toluene. In these spectra we have found no differences indicating occurrence of conformational changes induced by temperature changes or sample dissolution. The Raman spectra of pMOETMAI in the solid state and in aqueous solution, and the infrared spectrum of pMOETMAI in the solid state are shown in Fig. 8. The Raman spectrum of the solution does not exhibit any band indicating different conformational structure in the solution as compared to the solid state. The similarity of the Raman spectra of pMOETMAI and POETMAI in the solid and liquid states indicates that the structures of pMOETMAI and POETMAI are similar. Also the infrared spectra of pMOETMAI and POETMAI conform with the assumption that the structure of the quaternary (oxyethyl)trimethylammonium group in pMOETMAI is similar to that in POETMAI.

### CONCLUSION

By analysis of vibrational and NMR spectra it was shown that the quaternary (oxyethyl)trimethylammonium group in POETMAI and in pMOETMAI has the *g* conformational structure. In crystalline DMAEP, the 2-(dimethylamino)ethyl group also has the *g* structure. In liquid DMAEP and in solid pDMAEM, *t* conformational structures of the aminoethyl group are also present, but even here the contents of *g*

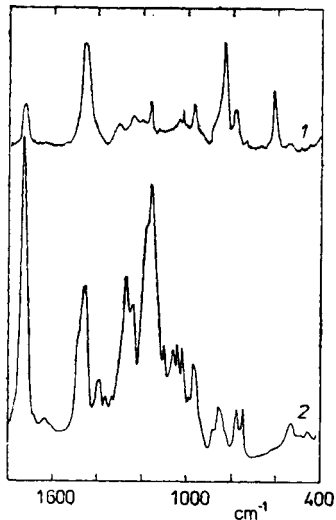


FIG. 7  
Raman (1) and infrared (2) spectrum of pDMAEM (sample I) in the solid state

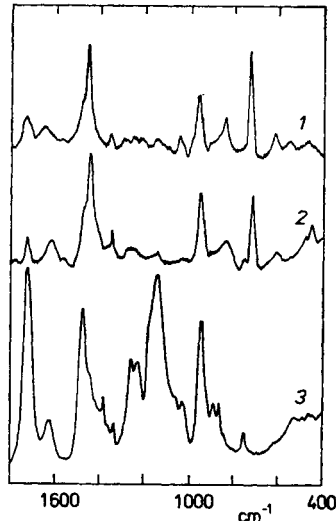


FIG. 8  
Raman (1, 2) and infrared (3) spectra of pMOETMAI; 1 solution, 2, 3 solid state

structures is larger than that of the **t** forms. By NMR and vibrational spectroscopic studies, the presence of various conformational structures of the ester groups, and conformer generation by rotation about the  $\text{CH}_2\text{—O}$  bond could not be established. In cyclic aminoethylester structures, the aminoethyl group must be in the **g** form. The high population of **g** structures of the aminoethyl group in DMAEP, pDMAEM and in their quaternary iodides indicate that cyclic structures of the aminoethylester group can exist in this type of compounds, and that they have to be considered in interpretations of their behaviour. As information on the generation of conformers by rotation about the  $\text{CH}_2\text{—O}$  bond could not be obtained, the geometrical structure of these cycles remains unknown.

## REFERENCES

1. Přádný M., Ševčík S.: *Makromol. Chem.* **186**, 111 (1985).
2. Přádný M., Ševčík S.: *Makromol. Chem.* **186**, 1657 (1985).
3. Štokr J., Schneider B., Doskočilová D., Ševčík S., Přádný M.: *Collect. Czech. Chem. Commun.* **52**, 1256 (1987).
4. Přádný M., Ševčík S.: *Makromol. Chem., Rapid Commun.* **5**, 37 (1984).
5. Ševčík S., Přádný M.: *Collect. Czech. Chem. Commun.* **51**, 206 (1986).
6. Pople J. A., Schneider W. G., Bernstein H. J.: *High-Resolution Nuclear Magnetic Resonance*. McGraw-Hill, New York 1959.
7. Mooney E. F., Winson P. H. in the book: *Ann. Rev. NMR Spectroscopy* (E. P. Mooney, Ed.), Vol. 2, p. 135. Academic Press, London 1969.
8. Štokr J., Sedláček P., Doskočilová D., Schneider B., Lövy J.: *Collect. Czech. Chem. Commun.* **46**, 1658 (1981).
9. Barfield M., Grant D. M.: *Adv. Magn. Reson.* **1**, 149 (1965).
10. Dirlikov S., Štokr J., Schneider B.: *Collect. Czech. Chem. Commun.* **36**, 3028 (1971).

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