

Unusual Phase Behavior of Some Poly(dialkoxyphosphazenes)

V. S. Papkov,* M. N. Il'ina, V. P. Zhukov, D. Ja. Tsvankin, and D. R. Tur

*Institute of Organo-element Compounds, USSR Academy of Sciences, 117334, GSP-1 Moscow, Russia**Received June 4, 1991; Revised Manuscript Received December 5, 1991*

ABSTRACT: An unusual transition from the mesomorphic state to the amorphous state has been found on cooling some poly(dialkoxyphosphazenes). This transition is proved by data obtained from thermomechanical analysis and optical and X-ray investigations. A generalized phase diagram is constructed for these polymers showing the influence of the alkoxy side group length on their glass transition temperatures, crystallization, and ability to form mesophases. The competition of interactions of the polar inorganic main chains and the side methylene chains has been proposed to be an important factor which controls the phase behavior of poly(dialkoxyphosphazenes).

Poly(dialkoxyphosphazenes) have attracted a good deal of attention in recent years not only as polymers with many technologically useful properties but also as an interesting means for exploring the mesomorphic state in flexible polymers containing no mesogens. The formation of thermotropic mesophases was first discovered in polyphosphazenes with trifluoroethoxy and some aryloxy side groups.¹⁻³ Recently, it was found that polyphosphazenes with alkoxy substituents also display the mesophase behavior, and the trend to form mesophases was suggested to be a common inherent feature of this class of polymers.^{4,5}

A specific characteristic of polyphosphazenes is a high flexibility of the inorganic backbone built up by polar $-P=N-$ bonds and framed by various pendant organic groups. In this respect polyphosphazenes are similar to linear siloxane polymers. It is of interest that both classes of polymers lend themselves to forming mesophases.⁶⁻⁸ The mesophases in these polymers are different from well-known liquid crystalline phases of polymers with mesogenic groups in the main or side chains. Presently, they are regarded by some authors as a special case of a partially disordered crystalline modification in thermodynamic equilibrium.^{3,7}

The origin of the mesomorphic state in polyphosphazenes is not yet entirely clarified. It was suggested that the transition of these polymers from the crystalline state to the isotropic melt via an intermediate mesomorphic state is due to the existence of a hierarchy of intra- and intermolecular interactions which are released step-by-step as the temperature increases.⁸ The competition between the interaction of the polar inorganic main chains and the interaction of the side organic substituents, which is promoted by high skeleton flexibility, was regarded as a possible reason for the appearance of the mesomorphic structure in polyphosphazenes.⁵

Our recent more detailed study on the mesophase behavior of poly(dialkoxyphosphazenes) revealed an unusual fact: the formation of a mesophase upon heating and the reverse conversion of the mesophase into the amorphous phase on cooling. This phenomenon seemed to be interesting regarding further elucidation of the origin of the mesomorphic state in inorganic polymers and, consequently, deserved additional consideration. The main features of this phenomenon obtained from DSC, X-ray diffraction, thermomechanical, and optical studies are described in the present paper.

Experimental Section

Materials. Poly(dialkoxyphosphazenes) $-(N=P(OR)_2)_n-$ with various alkoxy substituents ($OR = OCH_3, OC_2H_5, OC_3H_7,$

$OC_4H_9, OC_5H_{11},$ and OC_6H_{13}) were synthesized by replacement of Cl atoms in poly(dichlorophosphazene). The latter was prepared by polymerization of hexachlorocyclotriphosphazene $((NPCl_2)_3)$ (chromatographically pure) in sealed Pyrex tubes at 250 °C following a previously developed method ensuring the removal of residual water from the reaction system.⁹ The polymer had an intrinsic viscosity $[\eta] = 4.1$ dL/g in toluene at 25 °C and $M_w/M_n = 1.4$. The replacement of Cl atoms was carried out by treatment of $-(N=PCl_2)_n-$ with the sodium salt of a corresponding alcohol dissolved in the same alcohol, according to an earlier reported procedure⁵ that allows minimization of the presence of defects ($P-Cl$, $P-OH$, and $P=O$ groups) in the substituted polymers. Formed NaCl was removed by centrifugation of the polymer solutions in THF. Then polymers were precipitated into water. The yield of the polymers after reprecipitation was about 75%. Characteristics of the synthesized poly(dialkoxyphosphazenes) are listed in Table I. In this table and throughout this paper, the following abbreviation of the polymers is used: PDAP- C_n , where n means the number of C atoms in the alkoxy side group. Both reprecipitated samples and films cast from benzene solutions of the polymers were studied.

Techniques. To study the viscoelastic behavior of the PDAP samples, a thermomechanical method was used. Integral and differential thermomechanical traces, i.e., plots of compression strain (penetration) versus temperature under dead load and in the mode of alternating load (successive loading-unloading cycles), respectively, were recorded on a UIP-70M (USSR) thermomechanical analyzer permitting the measurement of the strain with an accuracy of 0.001 mm. Polymer samples about 1 mm thick were placed in a steel cup (1 mm in depth, 6-mm inner diameter). The diameter of a cylindrical indenter with the flat end connected to a quartz measuring probe was 2.52 mm. The applied compression stress varied from 0.02 to 0.1 MPa, depending on the compliance of the polymer samples. Under dead load the overall deformation (reversible plus irreversible) was monitored. The time regime used in the alternating mode of measurements (24 s under load followed by 96-s recovery in the unloaded state) allowed separation of the reversible strain at different temperatures. To avoid possible artifacts a small remaining stress was imposed on the sample in the unloaded state (about 0.0001 MPa). The heating/cooling rate was 5 °C/min.

DSC measurements were carried out at a heating rate of 8 °C/min using a DSM-2M (USSR) scanning calorimeter.

The X-ray diffractograms at different temperatures were taken on a DRON-2 (USSR) diffractometer with the use of filtered Cu $K\alpha$ radiation. Optical experiments were carried out under a polarizing microscope equipped with a photographic unit and a hot stage.

Results

Preliminary Basic Data on the Phase State of PDAP. The phase state of all investigated poly(dialkoxyphosphazenes) at 20 °C is given in Table I. These data are consistent with those of our recent study⁵ on the

Table I
Characteristics of Poly(dialkoxyphosphazenes)
-[P(OR)₂=N]_n- and Their Phase State at 20 °C

n	OR	notation	[η], ^a dL/g	P-Cl content, ^b mol %	P-OH content, ^c mol %	phase state ^d
1	OCH ₃	PDAP-C ₁	2.93	0.04	2.0	a
2	OC ₂ H ₅	PDAP-C ₂	6.50	0.06	2.7	a
3	OC ₃ H ₇	PDAP-C ₃	3.30	<0.02	0.2	m
4	OC ₄ H ₉	PDAP-C ₄	3.70	<0.03	0.1	m
5	OC ₄ H ₉	PDAP-C ₄ (a)	2.70	<0.03	2.7	a
6	OC ₅ H ₁₁	PDAP-C ₅	4.08	<0.03	0.1	m/a ^e
7	OC ₆ H ₁₃	PDAP-C ₆	5.62	<0.03	0.1	a

^a In THF at 25 °C. ^b According to the content of Cl atoms determined by coulometric titration. ^c Determined by NMR (see ref 5 for more detail). ^d Amorphous (a); mesomorphic (m). ^e Mesomorphic sample PDAP-C₅ was obtained by casting from benzene solution; amorphous sample PDAP-C₅(a) was prepared by precipitation.

influence of the alkoxy substituent size and structural macromolecule defects on the phase state of the polyphosphazenes. The following results of this study are important for further discussion:

(a) Poly(dialkoxyphosphazenes) are capable, in principle, of exhibiting mesomorphic behavior but the formation of mesophases is determined by the side group length and the content of defect sites in the macromolecules (in particular P-OH groups). Mesophases are found in poly(dialkoxyphosphazenes) with propoxy, butoxy, and pentoxy substituents if these polymers contain less than 0.2 mol % of the defect groups. At temperatures close to 200 °C they display the transition to the isotropic melt. Poly(dialkoxyphosphazenes) with methoxy and ethoxy side groups and those with propoxy and butoxy side groups containing about 2 mol % defects exist only in the amorphous state (see Table I).

(b) Despite the inherent symmetry of single-substituted polyphosphazene macromolecules, their crystallization in the case of short alkoxy side groups is likely hindered, and polymers from PDAP-C₁ to PDAP-C₆ failed to crystallize. Crystallization occurs only for a sufficiently long substituent, beginning with the heptoxy substituent.

In the mesomorphic state the studied poly(dialkoxyphosphazenes) are semisolid substances similar to soft waxes. In these polymers a birefringent domain could be observed between crossed polars (see Figure 1). In the amorphous state these polymers are optically isotropic rubber-like substances. The fundamental difference between diffractograms of mesomorphic and amorphous samples lies in the fact that the interchain mesomorphic reflections are stronger and more narrow than the corresponding first diffraction maxima in the latter case. The experimental width of the mesomorphic reflection at its half-height (half-width) recorded on the diffractometer was in all cases less than 0.5°, in contrast to the half-width of the corresponding amorphous halo, equal to more than 1.5°. This fact is illustrated by Figure 1 in which diffractograms for four investigated poly(dialkoxyphosphazenes) are presented (device broadening of the reflections is about 0.3°).

Thermomechanical Behavior. The results of our thermomechanical studies on noncrystallizable polyphosphazenes with side groups, varying from methoxy to hexoxy, showed the existence of several transitions in these polymers over a wide temperature range.

Integral thermomechanical traces, following the development of compression strain (penetration) with increasing temperature, are shown in Figure 2. For comparison, in Figure 2C DSC traces for mesomorphic samples of PDAP-C₃ and PDAP-C₄, and an amorphous sample of PDAP-C₂

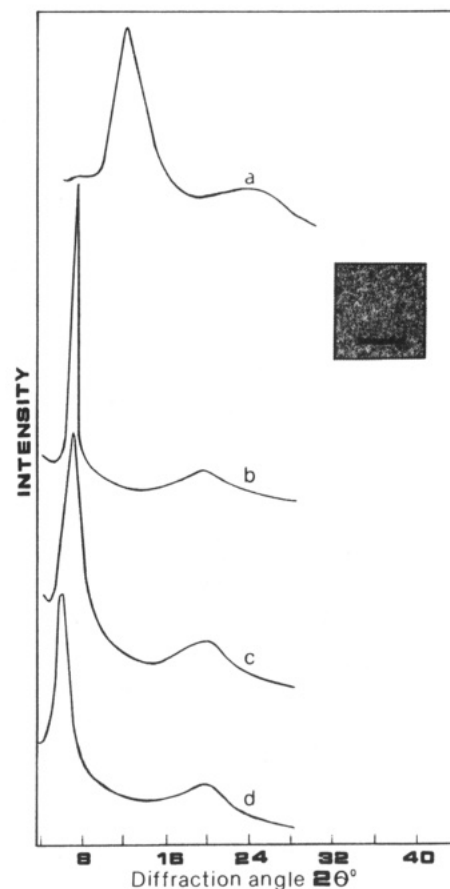


Figure 1. Diffractograms of some poly(dialkoxyphosphazene) samples at 20 °C: amorphous PDAP-C₁ (a); mesomorphic PDAP-C₄ (b); amorphous PDAP-C₄(a) (c); amorphous PDAP-C₆ (d). Insertion is a micrograph of the mesomorphic PDAP-C₄ sample in polarized light between crossed polars. Scale bar 200 μm.

are presented as well. In the glass transition region a drastic penetration is accompanied by a heat capacity jump. A similar heat capacity jump is also observed in all other investigated polymers. Compression strains occurring in this temperature region depend on the substituent length, phase state, and load applied. The glass transition temperatures determined from thermomechanical traces as temperatures corresponding to 1% strain proved to be somewhat higher than the glass transition temperatures referred to half heat capacity jump on DSC traces (see Table II). This is likely to be connected with a delay in the development of rubber elasticity of the samples with respect to the onset of high-level mobilities of the alkoxy side groups, which should provide the major input in the heat capacity jump in the glass transition region. It is also noted that, according to the DSC data,⁵ the glass transition temperatures of mesomorphic and amorphous samples of PDAP-C₃, PDAP-C₄, and PDAP-C₅ are practically the same.

In principle, all the integral thermomechanical traces can be divided into four sections. The first is the above-mentioned S-shaped section in the glass transition region. It is followed by a second S-shaped section with a small strain increase extending over a temperature range from approximately -50 to +30 °C and then by a third, practically linear section with a negative or positive gentle slope. The final fourth section is characterized by a drastic increase in penetration up to 100%, and it is more manifest in mesomorphic polymer samples. In this case the final section corresponds to the transition of the polymers to the isotropic melt (compare the thermomechanical and DSC traces in Figure 2B,C). Its position on the temper-

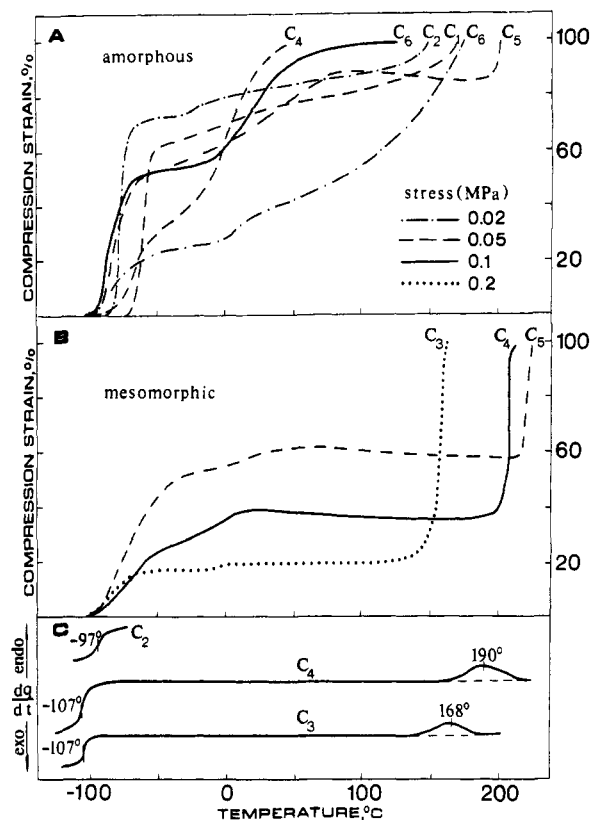


Figure 2. Integral thermomechanical traces (A,B) and schematic DSC traces (C) for amorphous and mesomorphic PDAP- C_n with various lengths of the substituent (C_n). Compression stresses applied are indicated in graph A. Heating rate is 5 °C/min for thermomechanical measurements and 8 °C/min in DSC runs.

Table II
Glass Transition Temperatures (°C) of
Poly(dialkoxyphosphazenes) (PDAP- C_n)

technique	1	2	3	4	5	6
TMA ^a	-72	-90	-103	-104	-104	-98
DSC ^b	-77	-97	-107	-107	-110	-104

^a Temperature corresponding to 1% penetration on integral thermomechanical trace at a heating rate of 5 °C/min. ^b Temperature corresponding to half heat capacity jump on DSC traces at a heating rate of 8 °C/min.⁵

ature axis only slightly depends on the compression stress. However, in the case of amorphous samples of PDAP- C_1 , PDAP- C_2 , PDAP- C_4 (a) containing defects, and PDAP- C_6 the fourth section is significantly shifted with increasing load to lower temperatures. This section can be even superposed upon the second one (see traces for PDAP- C_6 in Figure 2A).

To find out what part of the overall penetration at the different sections of the thermomechanical traces is reversible and originates from rubber elasticity of the polymer samples and what part is caused by their irreversible plastic flow, differential thermomechanical traces in the regime of loading-unloading were recorded (see Experimental Section). These sawtooth traces are given in Figures 3 and 4. They show compression strains occurring under loading (top points of the sawtooth traces) and recovery in the unloaded state achieved (bottom points).

Correspondingly, upper envelopes of such traces should characterize the overall penetration, and lower envelopes should point to the residual penetration developed under fixed experimental conditions. The height of each peak between both envelopes is in turn the reversible strain.

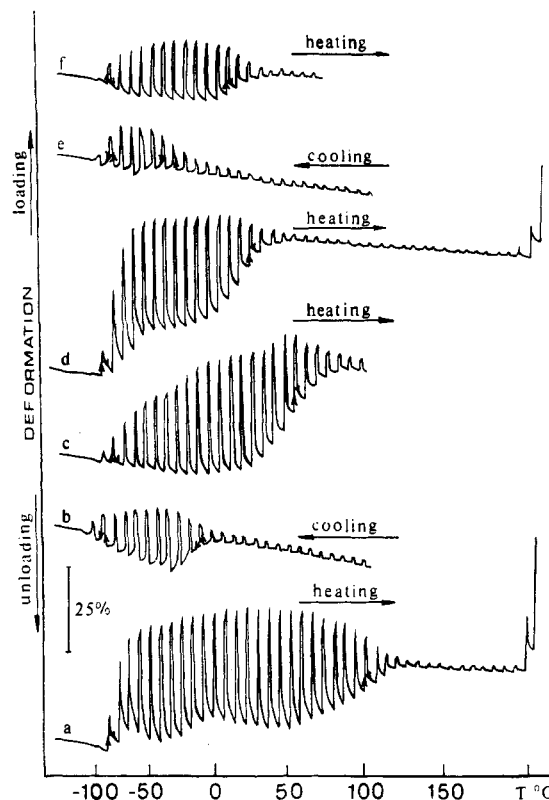


Figure 3. Differential thermomechanical traces (a-c) for amorphous PDAP- C_5 (a) sample and (d-f) for mesomorphic PDAP- C_5 sample. (a,d) First heating run; (b,e) cooling run after previous heating run up to 150 °C; (c,f) subsequent second heating run. Compression stress in loaded state is 0.04 MPa. Heating/cooling rate is 5 °C/min.

Some additional penetration kinetics measurements have shown that the chosen loading times at the applied compression stresses and used heating rates were sufficient for elastic and retarded elastic deformation to be realized practically completely. Longer duration of loading led mainly to the irreversible strain increase.

Consideration of the differential thermomechanical traces reveals unusual mechanical properties of poly(dialkoxyphosphazenes) capable of forming mesophases: namely, at lower temperatures they exhibit rubber elasticity and, respectively, undergo sufficiently large reversible strains but at higher temperatures, corresponding to the third section of the integral thermomechanical traces, the reversible strain can diminish by about 1 order of magnitude. This phenomenon is observed in a more striking fashion in poly(dipentoxyposphazene).

Depending on the preparation conditions (see Table I), samples of this polymer can exist at room temperature both in the mesomorphic state [films cast from polymer solutions with slow evaporation of solvents, designated PDAP- C_5] and in the amorphous state [reprecipitated samples, designated PDAP- C_5 (a)]. Such amorphous samples are metastable and can convert into the mesomorphic state when adding solvent with subsequent evaporation. However, at room temperature they can exist in the metastable amorphous state over a long period of time (at least 2 years) and even retain it after a heat treatment (see below). PDAP- C_5 (a) samples turned out to be very suitable for monitoring the above-mentioned phenomenon, and because of this we present data obtained for samples of the both types. Their differential traces are shown in Figure 3. As seen, the transition from the state which is characterized by large reversible deformation (i.e., by high penetration compliance) into the state related to small

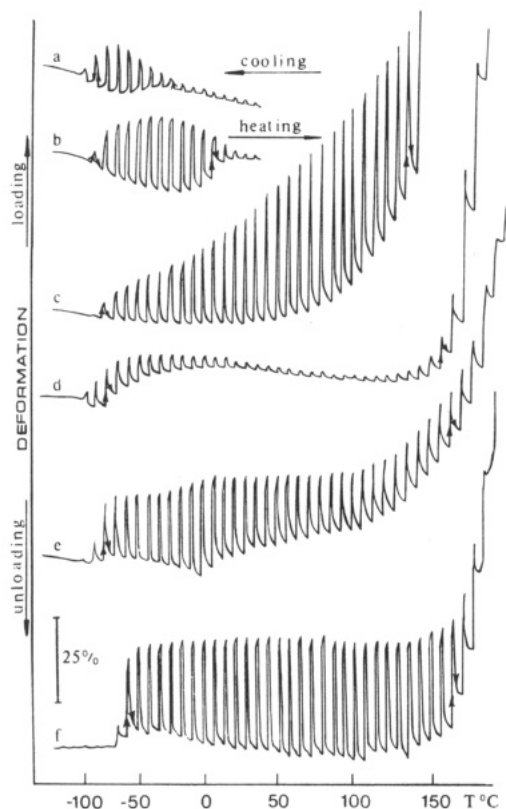


Figure 4. Differential thermomechanical traces for some PDAP- C_n samples: mesomorphic PDAP- C_4 (a,b); amorphous PDAP- C_4 (c); mesomorphic PDAP- C_3 (d); amorphous PDAP- C_6 (e); amorphous PDAP- C_1 (f). (a) Cooling run after previous heating run up to 80 °C; (b–f) heating runs. Compression stress in loaded state: 0.1 MPa (a,b,d); 0.02 MPa (c); 0.01 MPa (e,f). Heating/cooling rate is 5 °C/min.

reversible deformation is a common pattern of the thermomechanical behavior for the amorphous and mesomorphic samples. This transition is reversible and it can be monitored upon heating and upon cooling. According to the strains observed, estimates of the penetration compliance vary during the transition from the low-temperature state into the high-temperature state from 6×10^{-6} up to 3×10^{-7} MPa $^{-1}$.

In the amorphous sample this transition occurs at somewhat higher temperatures than in the mesomorphic sample, especially at first heating run. The reverse transition proceeds on cooling at a substantial supercooling in both cases and it is accompanied not only by reversible strain elevation but also by a jumpwise increase in negative penetration due to recovery of the sample (see traces b and e in Figure 3). The latter thermomechanical event is a manifestation of viscoelastic behavior of the polymer in the transition region. It arises because unrecovered reversible strain, stored during successive loading steps at a previous heating run (see traces a and d in Figure 3), recovers in the course of the reverse transition at lower temperatures, pointing to shorter relaxation times in the low-temperature state.

Mesomorphic PDAP- C_4 behaves in a similar way (see traces a and b in Figure 4). In mesomorphic PDAP- C_3 the above phenomenon manifests itself to lesser extent, although a trend to increase reversible strains at low temperatures is observed as well (see trace d in Figure 4).

Amorphous poly(dialkoxyphosphazenes), which are incapable of forming mesophases, viz., PDAP- C_1 , PDAP- C_2 , PDAP- C_4 (a) containing defects, and PDAP- C_6 , display another pattern of the thermomechanical behavior. As

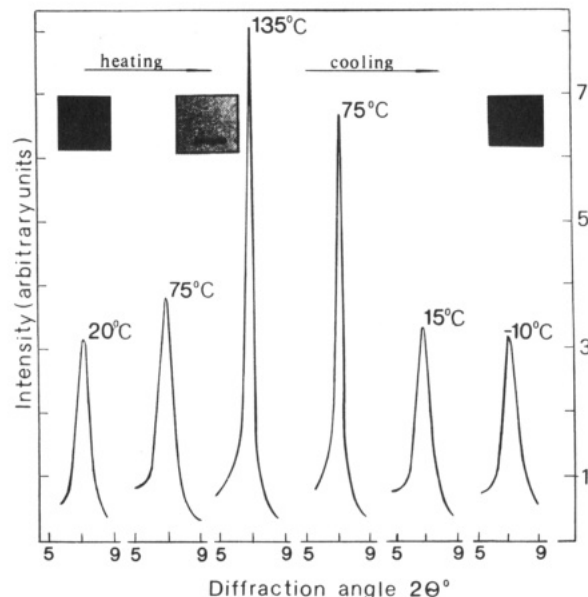


Figure 5. First X-ray diffraction maximum of amorphous PDAP- C_5 (a) sample at different temperatures. Insertions are optical micrographs of the sample at +20, +135, and -10 °C (from left to right) in the polarized light (crossed polars). Scale bar = 200 μ m.

seen from the differential thermomechanical traces for these polymers in Figure 4, there is no sharp change in penetration compliance in this case. A particular feature of all these traces is that above the glass transition temperature, starting with approximately -50 °C, an additional small increase in the reversible strain can be distinguished. The magnitude of reversible strain can level off with increasing temperature, as is the case for PDAP- C_2 and PDAP- C_6 , or increase constantly as illustrated by the trace for the PDAP- C_4 (a) sample. Finally, on further heating, the irreversible deformation due to viscous flow develops.

It should be noted, however, that a similar additional increase in reversible strain above -50 °C also occurs in the polyphosphazenes capable of forming mesophases. It is seen more clearly on inspection of the traces for the PDAP- C_5 samples (see Figure 3, traces a, c, and d). This is the process that is followed by the transition of the polymer into the above-described state characterized by a significantly lower compliance. Thus, the above-mentioned additional increase in reversible elastic strain above -50 °C is a common feature of the thermomechanical behavior of all the polyphosphazenes studied. This increase seems to be responsible for the appearance of the second S-shaped section on the integral thermomechanical traces (see Figure 2).

Optical and X-ray Data. Optical and X-ray investigations of the PDAP- C_5 (a) sample (amorphous at 20 °C) have shown that the above-mentioned pronounced decrease in penetration compliance on heating is accompanied by the appearance of birefringent domains along with an increase in intensity and decrease in half-width of the first X-ray diffraction maximum, characterizing interchain spacing (see diffractograms in Figure 5). Thus, the first amorphous halo converts into a sharp reflection similar to that observed for mesomorphic samples of this polymer. Upon subsequent cooling the original picture is reestablished; i.e., the birefringent domains disappear and the mesomorphic interchain reflection transforms back into the more diffusive amorphous halo. Intensity of the first diffraction maximum as a function of temperature is presented in Figure 6. A plot of half-width of the maximum versus temperature is shown here as well. The latter data

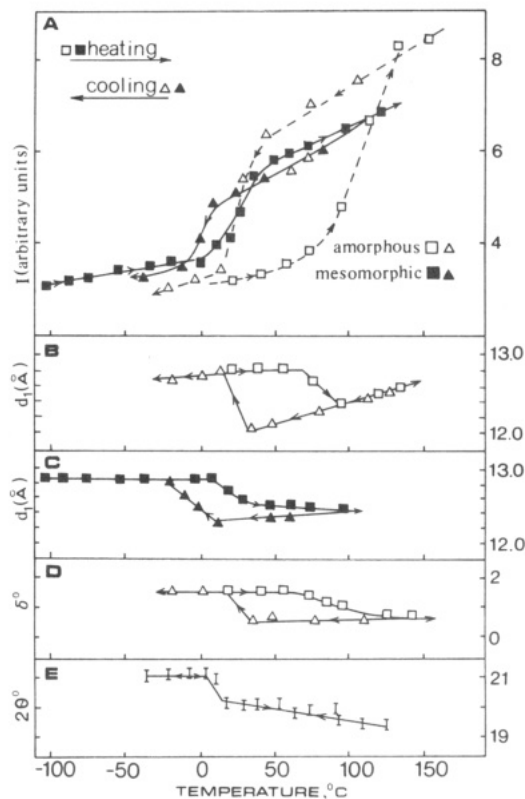


Figure 6. Intensity of the first X-ray diffraction maximum (A), corresponding interplanar spacing d_1 (B,C), half-width of the first diffraction maximum (D), and location of the second amorphous halo on the X-ray diffractogram (2θ) (E) as functions of temperature for amorphous and mesomorphic samples of PDAP-C₅. Graph E is common for amorphous and mesomorphic samples.

are rather qualitative since they are not corrected for device reflection broadening (about 0.3°). Figure 6 shows that in the course of the transition from the low-temperature state to the high-temperature state concurrently with jumpwise changes of the above parameters the interplanar distance d_1 varies in the same manner and its value becomes equal to that observed for mesomorphic samples.

In Figure 6 similar graphs for the mesomorphic PDAP-C₅ sample, cast from benzene solution, are also presented. They are consistent with the above thermomechanical data pointing to the existence of an analogous transition in the mesomorphic sample which is shifted to lower temperatures. Note that, according to optical data, the complete reverse transition in mesomorphic samples is kinetically hindered, and in such a sample, cooled to low temperature, some birefringent domains can remain a sufficiently long time, especially those of larger size and better perfection.

A similar jumpwise decrease in intensity of the first X-ray diffraction maximum and increase in its half-width upon cooling, accompanying drastic changes in penetration compliance, were also recorded for the mesomorphic PDAP-C₄ sample (see Figures 7 and 4). Reverse changes of these parameters take place on subsequent heating. In this case the transition to the low-temperature state is hindered as well, especially in the samples with more perfect morphology prepared via slow solvent evaporation. As a consequence, sometimes several preliminary cycles of heating-cooling for monitoring the reversibility of the transition were needed.

Thus, polyphosphazenes with side pentoxy and butoxy groups, containing very small amounts of defective groups, clearly exhibit the unusual transition from the mesomor-

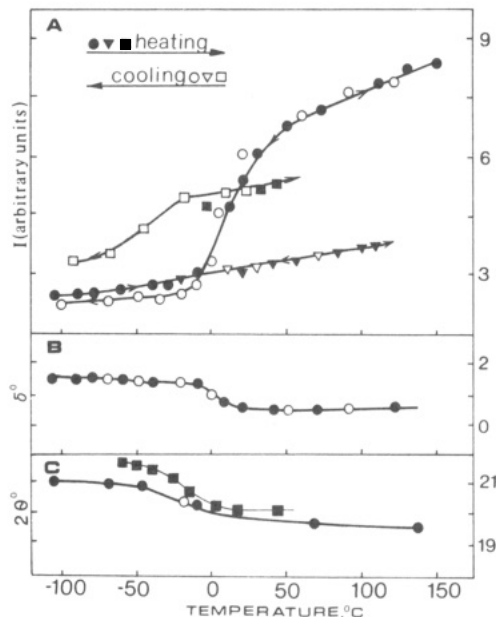


Figure 7. Intensity of the first X-ray diffraction maximum (A), its half-width (B), and location of the second amorphous halo on the X-ray diffractogram (2θ) (C) as functions of temperature for different PDAP-C_n samples: mesomorphic PDAP-C₄ [O,●]; amorphous PDAP-C₄(a) [Δ,▽]; amorphous PDAP-C₆ [□,■].

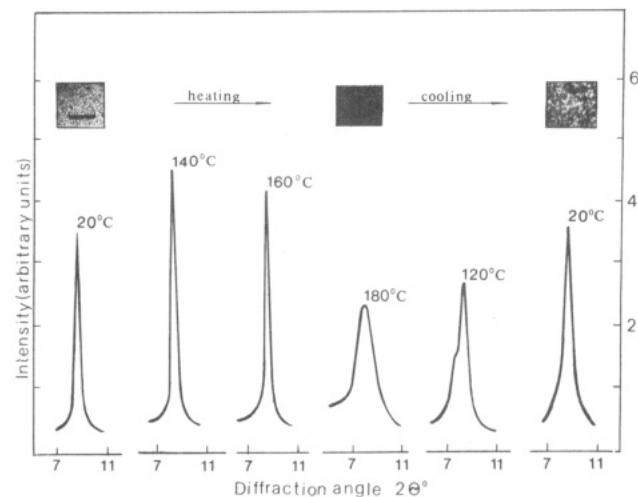


Figure 8. First X-ray diffraction maximum of PDAP-C₃ and its optical micrographs in polarized light between crossed polars at different temperatures. Scale bar = 200 μm .

phic state to the low-temperature disordered state on cooling and the reverse transition on subsequent heating. This disordered state seems to be referred to the amorphous one based on its structural, morphological, and mechanical characteristics.

In the case of the propoxy substituent this transition, according to the above thermomechanical data, is most hindered and it appears to proceed only to a slight degree. No jumpwise decrease in intensity of the mesomorphic reflection could be found unambiguously upon cooling mesomorphic samples of PDAP-C₃. The intensity varies reversibly with temperature and it increases practically linearly with increasing temperature up to the transition from the mesomorphic state to isotropic melt (see Figures 8 and 9). We note that the gradual reversible increase in intensity of the interchain diffraction maximum was found earlier not only for polyphosphazenes but also for poly-(organosiloxanes).¹⁰ This phenomenon was related to the decrease in the electron density at contact sites of adjacent cylindrical macromolecules due to the thermal expansion.

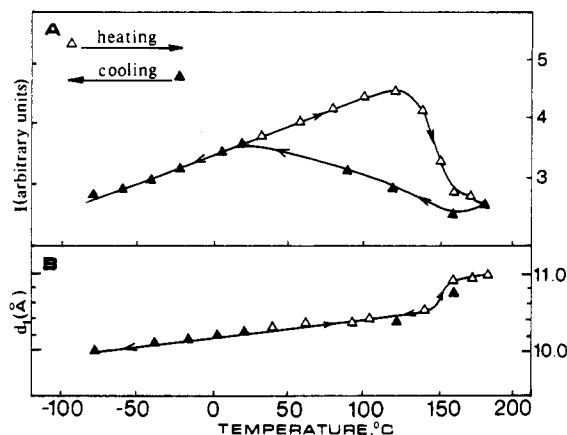


Figure 9. Intensity of the first X-ray diffraction maximum (A) and corresponding interplanar spacing d_1 (B) as functions of temperature for PDAP-C₃.

In the course of the transition of the mesomorphic sample of PDAP-C₃ to the isotropic melt, a jumpwise decrease in the intensity of the first diffraction peak, its broadening, and shifts to smaller diffraction angles 2θ occur. On subsequent cooling the reverse process occurs. This is proved by reestablishing the original X-ray diffractogram profile and by the reappearance of birefringent domains in the sample (see Figure 8).

In contrast, optical and X-ray data for amorphous samples of PDAP-C₁, PDAP-C₂, PDAP-C₄(a) containing defects, and PDAP-C₆, as well as the above thermomechanical data, reveal no transition of these polymers to the mesomorphic state on heating. Intensities of the first X-ray diffraction maximum in PDAP-C₄(a) and PDAP-C₆ samples versus temperature are plotted in Figure 7 (see their diffractograms in Figure 1). In the former polymer the intensity increases insignificantly with temperature. In the latter case the intensity of the first amorphous halo in a temperature range from -70 to 0 °C increases more steeply but its half-width remains practically unchanged.

Further inspection of the X-ray diffractograms has shown that in the temperature range from approximately -50 to +30 °C, which corresponds to the second S-shaped section of the integral thermomechanical traces, a jumpwise shift of the second amorphous halo, centered at a diffraction angle 2θ near 20°, takes place. The location of the second amorphous maximum on the X-ray diffractograms of PDAP-C₄, PDAP-C₅, and PDAP-C₆ samples as a function of temperature is shown in Figures 6 and 7. The jumpwise shift of the second amorphous halo is reversible and proceeds on cooling practically without hysteresis in contrast to the changes of the first diffraction maximum considered above.

As known, the second amorphous halo results usually from both interchain and intrachain spacings. Thus, taking into account that the interchain distances in all the PDAP remain practically constant over this temperature range, one can suggest that such a shift of the second amorphous halo is connected with changes in main chain and/or side group conformations. As shown in Figures 6 and 7, on heating, the above-described low-temperature amorphous phase-mesophase transition follows these proposed conformational changes with a certain temperature delay (especially noticeable in the case of PDAP-C₅(a)). Consequently, one can suppose that the conformational transformations are the first step of a two-stage amorphous phase-mesophase transition, the second step of which consists of self-organization of macromolecules

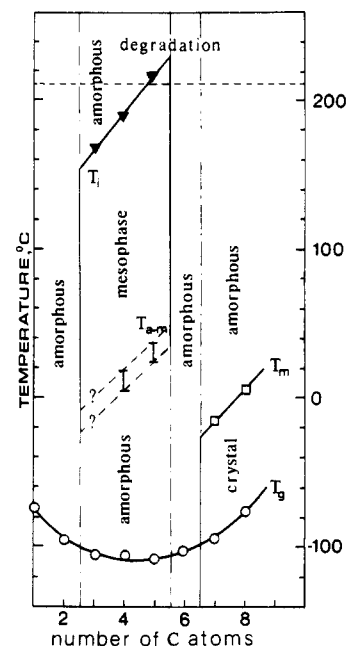


Figure 10. Generalized phase diagram for PDAP-C_n with various number n of C atoms in the alkoxy side group. PDAP-C₁ and PDAP-C₂ are denoted as amorphous conditionally since they contain defect groups in their structure (see text).

in parallel packing (or their disordering during the reverse transition). In the case of poly(dialkoxyphosphazenes) incapable of forming mesophases the above-mentioned conformational changes appear to result only in another pattern of viscoelastic behavior of the polymer.

Discussion

On the basis of the above data and those on the melting points of crystallizable poly(diheptoxyphosphazene) and poly(dioctoxyphosphazene) reported earlier,⁵ a generalized phase diagram for poly(dialkoxyphosphazenes) can be outlined. This diagram is constructed in Figure 10. It is obviously useful for the consideration of the influence of the side alkoxy group on the phase state of these polymers.

On this diagram the temperatures of the mesophase-isotropic melt transition (isotropization) T_i are referred to the temperatures of the corresponding endothermal peaks on the DSC traces for PDAP-C₃ and PDAP-C₄ (see Figure 2C) and to the temperature of the onset of abrupt penetration on the fourth section of the integral thermomechanical traces for PDAP-C₅ (see Figure 2B). The latter is connected with the fact that the isotropization of the mesomorphic PDAP-C₅ samples occurs at temperatures above 200 °C where destructive processes begin. This complicates the unambiguous separation of the endothermal isotropization peak on the DSC traces.

To picture this fact a tentative temperature boundary of a noticeable decrease in the intrinsic viscosity of the polyphosphazenes due to the destruction is marked on the diagram by a horizontal dashed line. Temperatures of the low-temperature amorphous phase-mesophase transition T_{a-m} in PDAP-C₅, PDAP-C₄, and PDAP-C₃ are related to the temperatures at which the upper and lower envelopes of the differential thermomechanical traces strive to come together (see Figures 3 and 4). Since this transition (as well as the reverse one) seems to be kinetically hindered and its thermomechanical manifestations extend over a rather wide temperature range, we mark by two broken lines in Figure 10 a temperature interval in which it is expected to occur.

In the case of PDAP-C₃ the determination of the temperature of the low-temperature disordered phase-mesophase transition is especially difficult as the reverse transformation proceeds on previous cooling only to a small extent. In this connection the proposed temperature interval of the transition in PDAP-C₃ is indicated by two question marks to stress the not fully clarified situation.

Polyphosphazenes with methoxy and ethoxy side groups are designated on the diagram as amorphous polymers over the whole temperature range. However, the investigated samples of these polymers contained sufficient amounts of defective groups in their structure to prevent, in principle, the appearance of mesophases.⁵ Therefore, the question about their phase state still remains open.

The temperature region of the existence of the poly(dialkoxyposphazenes) in the glassy state is bounded by a solid line passing over the glass transition temperatures T_g determined by means of scanning calorimetry (see Table II and ref 5). The boundary line between the crystalline state and the amorphous state for crystallizable PDAP-C₇ and PDAP-C₈ is drawn over their melting points T_m , also measured by DSC.⁵ Indeed, real samples of these polymers in the crystalline state also contain the amorphous phase, although their crystallinity is very high (>0.9 in PDAP-C₈).⁵

The phase diagram in Figure 10 demonstrates the influence of the alkoxy substituent length on the phase behavior of the polyphosphazenes. First of all it reveals that the appearance of mesophases is observed only in a certain range of the substituent length, viz., from 3 to 5 C atoms in the alkoxy groups, that corresponds to a broad minimum of the glass transition temperatures. With further increasing number of C atoms in the side groups the glass transition temperature markedly increases and the mesomorphic state cannot be realized. However, starting with 7 C atoms in the side alkyl chain, the polyphosphazenes gain the ability to crystallize. Such a correlation between the influence of the side group length on the glass transition temperature of poly(dialkoxyposphazenes) and on their phase behavior may be thought to have a real physical basis.

Earlier we suggested⁵ that this correlation could arise because the same factors are responsible for macromolecular packing and for the overall intermolecular interaction, determining the glass transition temperature. The first of them is the intermolecular interaction of inorganic main chains, consisting of polar $\text{P}=\text{N}$ bonds, and/or polar $\text{P}-\text{O}-\text{C}$ bonds in the side groups. The second one is the intra- and intermolecular interaction of the alkyl side chains. The contribution of the latter factor to the free energy of the system should grow with increasing number of C atoms in the side group. However, simultaneously their screening effect, which compensates dipole-dipole interchain interaction, may become more pronounced. It is the superposition of these two interactions that appears to give rise to the occurrence of the minimum in the plot of T_g versus side group length. With further increases in the number of CH_2 groups the contribution to the free energy from the interaction of the side alkyl chains should become predominant and, therefore, govern both the packing of macromolecules and their self-organization kinetics. In fact, the mesomorphic structure in the case of the hexoxy substituent is not observed, and poly(dialkoxyposphazenes) with larger substituents already crystallize due to the realization of the energetically more favorable all-trans conformation of the methylene side chains.⁵ In this respect the crystallizable polyphosphazenes with long alkoxy side groups resemble the crys-

tallizable hydrocarbon comblike polymers. The latter, however, crystallize at a greater length of the side chain. For example, poly(vinyl alkyl esters) crystallize starting only with 11 C atoms in the alkyl side group.¹¹

The existence of the low and upper critical temperatures of the mesophase behavior of poly(dialkoxyposphazenes) may also be explained within the framework of a model suggesting two types of interaction of polyphosphazene macromolecules, i.e., their biphilic character.

It is likely possible using such conditional terms as "micibility" and "separation" of intermolecular contacts of different types (proposedly resulting from dipole-dipole interaction and interaction between side methylene chains). Consequently, the mesophase-isotropic melt transition at the upper critical temperature can be attributed to release of the intermolecular interactions and mixing intermolecular contacts of different origins due to a gain in entropy. This is a first-order transition which is accompanied by a corresponding endothermal effect (see Figure 1; the heat of transition is about 2.5 and 4 J g⁻¹ for PDAP-C₄ and PDAP-C₃, respectively⁵).

The mesophase-low-temperature amorphous phase transition may in turn be explained by forced mixing the above contacts owing to arising additional specific interactions at lower temperatures. Such a suggestion implies, in essence, an enthalpic driving force of the transition. However, we could not recognize unambiguously any thermal event on the DSC traces in the transition region. This fact can supposedly be connected with a too small heat of transition and/or with a rather wide temperature range of heat evolution.

Finally, the mesomorphic structure could be related to the separation of the interaction sites of different types. Their competition can be expected to control a proper packing of the macromolecules and properties of the mesophase. In principle, this approach is derived from a speculative consideration of the driving force of mixing and demixing in some bicomponent systems with a LCST and UCST. Obviously, it is very oversimplified but may be useful as a first step to the development of a more realistic model.

Presently, it is impossible to specify the type of proposed interaction responsible for the transition to the amorphous state at lower temperatures. However, it can be supposed that conformational transformations of the methylene side chains and corresponding subsequent changes in their interaction and packing underlie this transition. At least, in such a way may be interpreted the above-described jumpwise shift of the second broad diffraction maximum on X-ray diffractograms of poly(dialkoxyposphazenes) (see Figures 6 and 7). At room temperature and somewhat higher temperatures this amorphous halo is located at a diffraction angle 2θ of about 20° ($d_2 = 4.5$ Å) for all the polypolyphosphazenes starting with PDAP-C₄ (see Figure 1). Note that a similar second amorphous halo is also observed for amorphous samples of such comblike polymers as poly(*n*-alkyl acrylates), poly(alkylethylenes), and poly(vinyl alkyl esters) and for polyethylene melt.¹¹ The interplanar spacing $d_2 = 4.5$ Å is proposedly considered as a parameter characterizing the packing of conformationally disordered methylene chains. On crystallization of these comblike polymers a crystalline reflection about 4.2 Å instead of the above amorphous halo appears, and it is ascribed to hexagonal packing of the methylene side chains which have the planar all-trans conformation.¹¹ A similar change of the X-ray diffractogram profile on crystallization of PDAP-C₇ and PDAP-C₈ was also observed.⁵

As shown in Figures 6E and 7C, with decreasing temperature the second amorphous maximum in the diffractograms of poly(dialkoxyposphazenes) with butoxy and pentoxy substituents is shifted jumpwise to $2\theta = 21^\circ$ ($d_2 = 4.2$ Å). In propoxy-substituted polymer the center of a similar amorphous halo is shifted from $2\theta = 21^\circ$ to $2\theta = 22^\circ$. Taking into account the above-mentioned data on the comblike polymer structure, it can be assumed that the content of trans conformations of the bonds in the methylene side chains increases at low temperatures and their partial or full straightening occurs. In the latter case crystallization should be expected, and it actually proceeds in heptoxy- and octoxy-substituted polymers. In polyphosphazenes with propoxy, butoxy, and pentoxy side groups, judging by the small shift of the first interchain diffraction maximum (see Figures 6 and 7), only a partial straightening of the methylene side chains may take place. This gives rise to a new denser, but still distorted, packing of the side groups. Nevertheless, such a packing seems to be already capable of disturbing the parallel arrangement of macromolecules and, thus, results in the mesophase-amorphous phase transition.

If the above suggestions are valid, one can expect that the low-temperature amorphous phase is different from the high-temperature amorphous phase (isotropic melt). Another peculiar feature of this amorphous phase is that its Gibbs free energy should be, in principle, lower than that of the mesophase. Such an unusual, at first glance, situation can apparently arise because of the higher contribution to the free energy from the side group packing than from a parallel alignment of the macromolecules in the low-temperature region.

In the framework of the concept developed it is also reasonable to expect that the existence of some specific intra- and/or intermolecular interactions and steric hindrances (including chain entanglements) can prevent or retard mesophase formation if the driving force of this process is sufficiently small. Such a situation is apparently the case for PDAP-C₅(a), PDAP-C₄(a), PDAP-C₂, and PDAP-C₁. The last three amorphous polymers contained about 2 mol % of defect P-OH groups capable, in principle, of forming coordination links. However, it is not excluded that PDAP-C₁ and PDAP-C₂, even containing no defects, cannot convert into the mesomorphic state at all since strong enough dipole-dipole interchain interaction is possible in the case of short methyl and ethyl side groups that can suppress biphilic manifestations of the macromolecules. This question can be elucidated entirely only after overcoming all synthetic difficulties in preparation

of these polymers without defects.

Conclusions

The occurrence of mesophases in poly(dialkoxyposphazenes) with only certain lengths of the side group, the unusual transition of these polymers at low temperatures from the mesomorphic state into the disordered state (denoted as the amorphous state), and their ability to crystallize starting only with the heptoxy substituent point out that the competition between interactions of side groups and the polar main chains is undoubtedly a factor that controls the self-organization of the macromolecules.

Another important factor seems to be the inorganic backbone flexibility, which permits all these interactions to be realized. The influence of the latter factor is expected to be more significant if the interaction is not very strong as it, indeed, takes place in poly(dialkoxyposphazenes).

On the other hand, certain restrictions of mobilities of the side groups attached to polar phosphazene units of the main chain by means of the polar P-O-C bridge can apparently produce a stabilizing effect on specific interactions and, thus, confer upon the side group or the whole repeat chain unit some mesogenic properties.

With respect to further development of such a concept of the polyphosphazene mesophase behavior a more detailed investigation of various specific interactions of the side groups and the main chains as well as their conformational analysis in different phase states are needed.

References and Notes

- (1) Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44.
- (2) Schneider, N. S.; Desper, C. R.; Singler, R. E. *J. Appl. Polym. Sci.* **1976**, *20*, 3087.
- (3) Schneider, N. S.; Desper, C. R.; Beres, J. J. *Polymer Liquid Crystals*; Academic: New York, 1976; Chapter 9.
- (4) Tur, D. R.; Papkov, V. S.; Dubovik, I. I.; Provotorova, N. P.; Tsvankin, D. Ja.; Slonimsky, G. L. *Vysokomol. Soedin.* **1989**, *B31*, 483.
- (5) Tur, D. R.; Provotorova, N. P.; Vinogradova, S. V.; Bakhmutov, V. I.; Galakhov, M. V.; Dubovik, I. I.; Zhukov, V. P.; Tsvankin, D. Ja.; Papkov, V. S. *Makromol. Chem.* **1991**, *192*, 1905.
- (6) Beatty, C. L.; Pochan, J. M.; Froix, M. F.; Hinman, D. F. *Macromolecules* **1975**, *8*, 547.
- (7) Wunderlich, B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60/61*, 1.
- (8) Godovsky, Ju. K.; Papkov, V. S. *Adv. Polym. Sci.* **1989**, *88*, 129.
- (9) Korshak, V. V.; Vinogradova, S. V.; Tur, D. R.; Kazarova, N. N.; Gilman, L. M. *Acta Polym.* **1979**, *30*, 245.
- (10) Tsvankin, D. Ja.; Levin, V. Ju.; Papkov, V. S.; Zhukov, V. P.; Zhdanov, A. A.; Andrianov, K. A. *Vysokomol. Soedin.* **1979**, *A21*, 2126.
- (11) Plate, N. A.; Shibaev, V. P. *Comb-like Polymers and Liquid Crystals*; Plenum Press: New York, 1987; Chapter 1.