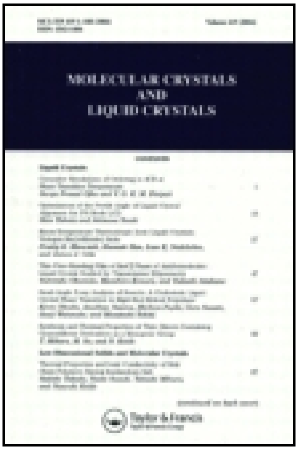

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Induction of Mesomorphic Properties in Poly(propylene imine) Dendrimers and their Model Compounds

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INDUCTION OF MESOMORPHIC PROPERTIES IN POLY(PROPYLENE IMINE) DENDRIMERS AND THEIR MODEL COMPOUNDS

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The lyotropic phase behaviour of selected dendrimers with non-mesomorphic peripheral units, i.e. decyloxybenzoyl substituted poly(propylene imine) dendrimers as well as model compounds of their main parts, i.e. decyloxybenzoyl substituted alkylamines and also derivatives of 1,4,7-triazacyclononane, has been studied.

For the first time, the induction/variation of mesomorphic properties in binary systems of these dendrimers or of related model compounds with suitable organic solvents has been established.

Keywords: dendrimers; lyotropic mesomorphism; organic solvents

INTRODUCTION

Dendrimers are super-branched synthetic macromolecules occupying intermediate space between low-molecular compounds and polymers. Each dendritic molecule, which at the same time is a nano-particle, can be considered as a "monomolecular micelle" [1].

Thermotropic mesomorphism of amphiphilic poly(propylene imine) dendrimers of the 1st to the 5th generation with a "radial segment structure" as well as substituted alkylamines, which are model compounds for

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the end-groups of dendrimers, has been studied recently [2]. It was found that with increasing generation or branching of lateral substituents the stability of mesophases increases with respect to the crystalline phase.

Despite the existence of a numerous variations of dendrimer structures in general, including those with mesomorphic properties, practically no attempt has been undertaken to study the properties of dendrimers with solvents from the mesophase induction point of view.

As found for disc-like mesogens with rigid cores, using a solvent may not only to widen the temperature range of an existing thermotropic mesophase, but may even induce the mesomorphic state in thermotropically non-mesomorphic compounds. Basing on this idea, it was interesting to apply an accumulated experience for induction/variation of mesomorphic properties for the compounds similar in molecular shape, but having no clearly expressed core. In order to achieve this goal a homological series of derivatives of 1,4,7-triazacyclononane **1**, poly(propylene imine) dendrimers **4** and a number of decyloxybenzoyl substituted alkylamines as model compounds for main parts (central fragment or end-groups) **2–3** of above mentioned dendrimers were studied in binary mixtures with organic solvents.

Recently we have established two most promising ways for lyomesophase appearance: i) binary systems of such compounds with cyclic solvents, ii) binary systems with linear alkanes of the same number of carbon atoms as in the paraffinic part of disk-like compounds [3]. This determined the choice of the used solvents.

EXPERIMENTAL

The synthesis of studied 1,4,7-triazacyclononanes, dendrimers of different generations as well as model compounds of their end-groups were synthesised as described before [2].

All the organic solvents: chloroform, *n*-hexane, cyclohexane, octane, decane, decanol, DMF, DMSO, THG – commercial available products of E. Merck Ltd. Darmstadt, Germany were used without further purification.

The lyotropic mesomorphism was studied by polarising optical microscopy (methods of contact preparations and building of phase diagrams) using a "Leitz Laborlux 12Pol" microscope equipped with a "Mettler FP 82" hot stage, heating rate 2°C/min. The texture photographs were taken with a 24 × 36 mm microscope camera and a photoautomat "Wild MPS 51".

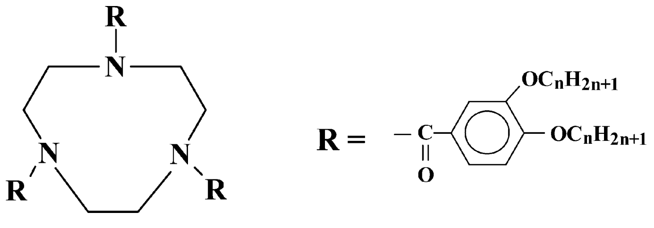
RESULTS AND DISCUSSION

Earlier [3] it has been shown that lyotropic mesophases for discotic compounds could be induced with the help of a suitable solvent, even in the case of non-mesomorphic materials. Moreover, using benzene or cyclohexane derivatives [3] we showed that saturated six-membered central core is more favourable for displaying of lyotropic mesomorphism.

I. Lyotropic Mesomorphism of 1,4,7-Triazacyclononane Derivatives

1,4,7-triazacyclononane derivatives **1** (Fig. 1) possessing *nine*-membered flexible hetero-atomic central fragment were chosen as “transitional” compounds from low-molecular discostic mesogens (e.g., cyclohexane esters [3]) to dendrimers. Moreover, compounds of series **1** have the same lateral substituents as dendrimers, which will be described below.

The research on induction/variation of lyotropic mesomorphism showed, that it is not possible to induce any lyomesophase for the two first *non-mesogenic* [4] homologues **1a–b** with the used solvents. For *monotropic* homologue **1d** (n = 6) the *enantiotropic* lyomesophase in binary systems with cyclohexane was obtained. For mesomorphic homologue **1c** original thermotropic mesophase is kept intact but in lyotropic state the phase transition temperature into isotropic state is lowed (54 and 47 °C, correspondingly). For the rest of thermomesomorphic members of homological series **1** (**1e** and **1f**) in binary systems with the hydrocarbons mentioned above, an expansion of temperature diapason of the lyomesophase existence was observed: at cooling the lyomesophase remains the same up to room temperature. Besides, during cooling in lytropic systems unlike thermotropic state of **1c, d** and **e** the occurrence of two types of textures was observed: a non-geometrical texture, which accompanied by spherulites and/or Schlieren-like texture (Fig. 2). It means that there could be several *polymorphic* modifications instead of thermotropic *mono*-mesomorphism. In a number of cases the formation of glass state was detected for compounds **1c–f** in mixtures with the solvents. However, this process could be turned around in the next cycles of heating.



1a: n=1; **1b:** n=3;
1c: n=5; **1d:** n=6;
1e: n=8; **1f:** n=10

1

FIGURE 1 Molecular structure of 1,4,7-triazacyclononane derivatives.

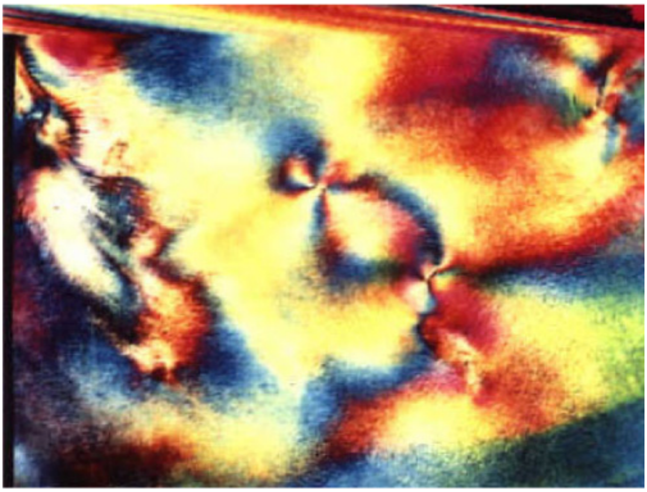


FIGURE 2 Microphotograph of Schlieren-like texture of **1e**/octane contact preparation at T = 34,9°C on heating, crossed polarizers, × 250. (See COLOR PLATE I)

Thus, the conclusion/rule achieved before (saying that for columnar lyomesophase formation by disc-like compounds is optimal to have the cyclic solvent) is confirmed for compounds of series **1**.

II. Lyotropic Mesomorphism of Model Compounds for the Studied Dendrimers

Usually mesomorphic properties are displayed by dendrimers possessing mesogenic end-fragments or mesogenic core. In the case of poly(propylene imine) dendrimers **4**, which we describe in this paper, the end-fragments as well as the dendritic matrix are *non-mesomorphic*. That is why before studying the lyotropic mesomorphism of dendrimers **4** it was interesting to test the lyotropic mesomorphism of their model compounds (Fig. 3), which present the main parts of dendrimers (central core, end-fragment) with the help of suitable solvents from the induction of mesomorphic properties point of view.

The thermotropic mesomorphism of model compounds of the end-groups **2** of dendrimers as well as of the central fragment **3** (Fig. 3): 3,4-di-decyloxybenzoyl substituted propylamine (**2a**), 3,4,5-tridecyloxybenzoyl substituted propylamine (**2b**), 4-decyloxybenzoyl di-substituted 1,4-diaminobutane (**3a**) and 3,4-didecyloxybenzoyl disubstituted 1,4-diaminobutane (**3b**) was studied earlier [2].

For non-mesomorphic compounds **2a** or **2b** it is characteristic to have *induction* of mesomorphic state (Fig. 4) with a wide range of solvents

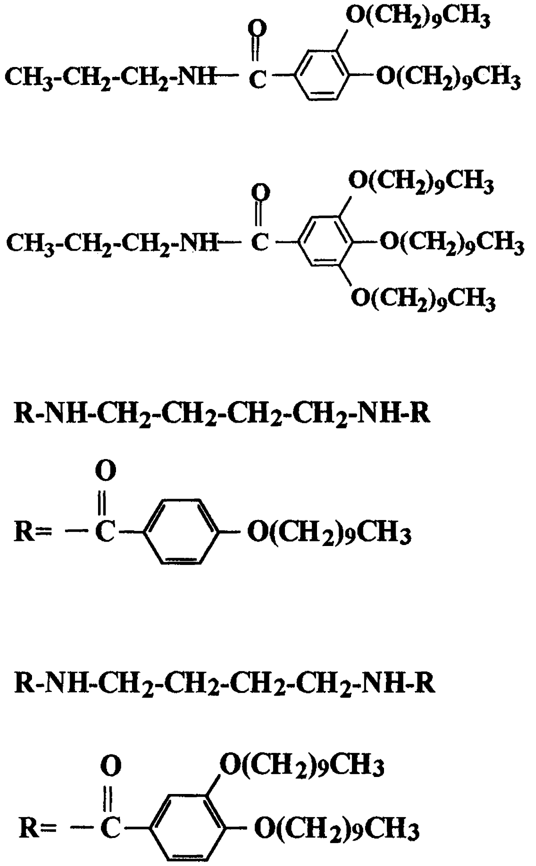


FIGURE 3 Model compounds for the *end-groups* **2a-b** and *central fragment* **3a-b** of the studied dendrimers.

(Table I). The type of textures (non-geometrical, broken fan-like or Schlieren) as well as lyomesogenity depends on the used solvents.

Unfortunately, **3a** does not display lyomemorphic properties, though **3b** displays lyomesophase (Table I) in binary mixtures with THF or chloroform. The type of the texture and calamitic character of molecules witness in favour of their lamellar supermolecular packing in lyomesophase.

III. Amphotropic Properties of Poly(propylene imine) Dendrimers

Poly(propylene imine) dendrimers of different generations **4a** (1-K1), **4b** (1-K3), **4c** (3-K2), **4d** (4-K1), **4e** (5-K2) (Fig. 5) together with one

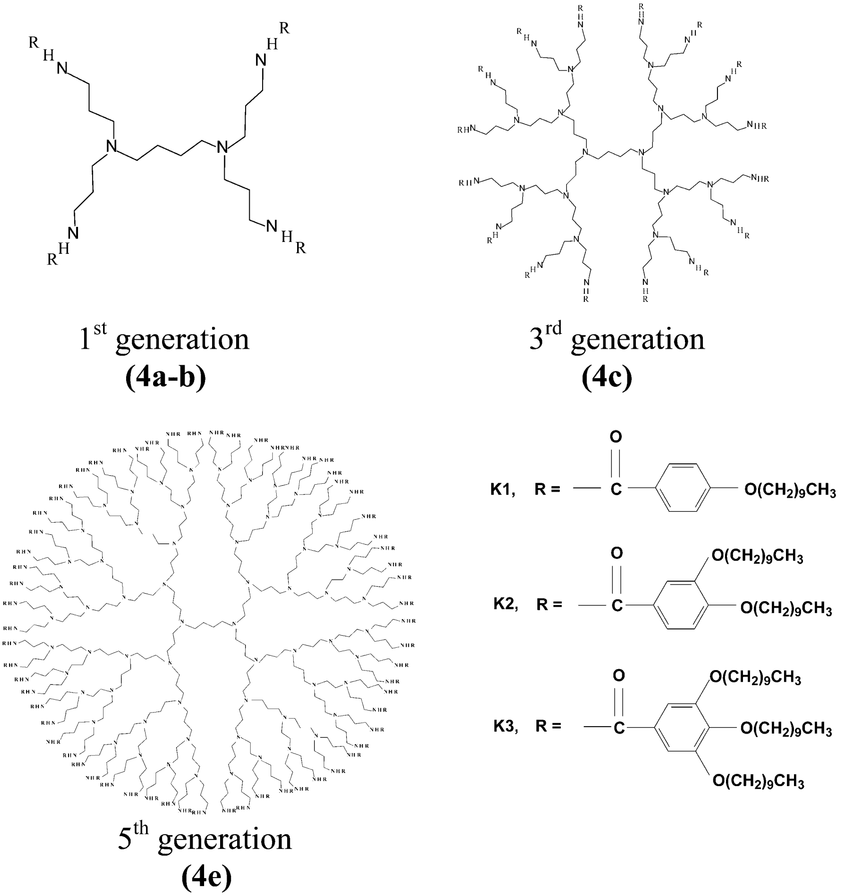
FIGURE 4 Microphotograph of the contact preparation of **2b** with hexane, T = 20°C, crossed polarizers, ×250. (See COLOR PLATE II)

100%-protonated analogue **4f** (3-K2·14DSA) were chosen to investigate their lyomesomorphic properties in binary mixtures with organic solvents. First of all, the possibility of induction/variation of mesomorphic properties using suitable solvent was considered. From the point of influence of

TABLE I The Lyotropic Mesomorphism in Contact Preparations of Thermotropically Non-mesomorphic Model Compounds **2–3** with Organic Solvents. T = 20°C

	Solvents							
Compounds	$CHCl_3$	n-hexane	Cyclo-hexane	Decane	Decanol	THF	C_2H_5OH $CHCl_3$ (5:1)	DMFA
2a	Lyo-mes	Lyo-mes	Lyo-mes	Cr + Solv	Cr + Solv	Lyo-mes	Cr + Solv	Cr + Solv
2b	Lyo-mes	Lyo-mes	Lyo-mes	Cr + Solv	Cr + Solv	Lyo-mes	Lyo-mes	Cr + Solv
3a	Cr + Solv	Cr + Solv	Cr + Solv	Cr + Solv	Cr + Solv	Cr + Solv	Cr + Solv	Cr + Solv
3b	Lyo-mes	Cr + Solv	Cr + Solv	Cr + Solv	Cr + Solv	Lyo-mes	Cr + Solv	Cr + Solv

Cr = crystalline phase, Lyomes = lyomesophase, Solv = solvent.



1st generation
(4a-b)

3rd generation
(4c)

5th generation
(4e)

FIGURE 5 Examples of molecular structure of poly(propylene imine) dendrimers **4** of 1st, 3rd and 5th generations and their end-fragments.

dendrimer molecular structure on ***lyotropic mesomorphism*** the following aspects were taken in account:

1. increasing of generation number of dendritic molecule: **4a** (1-K1) and **4d** (4-K1) or **4c** (3-K2) and **4e** (5-K2);
2. branching of lateral substituents; for this study dendrimers of the same generation but with different number of aliphatic chains in terminal groups of lateral substituents were chosen, for example: **4a** (1-K1) and **4b** (1-K3);
3. effect of protonation: **4c** (3-K2) and **4f** (3-K2·14DSA).

Survey of the Thermotropic Mesomorphism of Studied Dendrimers [2].

The data on themotropic mesomorphism of studied dendrimers are summarised in Table II.

Poly(propylene imine) dendrimer of the first generation, **4a** (1-K1), is thermotropically non-mesomorphic. Therefore, it was interesting to induce the mesomorphic properties with the help of the solvent.

The analogue **4b** (1-K3) with three aliphatic chains in lateral substituents forms columnar rectangular thermotropic mesophase of disordered type (Col$_{rd}$) at high temperature. The appearance of polymorphic modifications could be reached in mixtures with the solvents.

Poly(propylene imine) dendrimer of the 3rd generation, **4c** (3-K2), displays a thermotropic hexagonal columnar mesophase (Col$_{hd}$). In this case, it could be interesting to realise the phase transition to the other (e.g. nematic) lyomesophase, using an organic solvent.

With the aim of increasing of polar/apolar contrast improving the microsegregation processes and decreasing of flexibility of dendritic matrix the protonation of **4c** due to interaction with decyl sulfonic acid has been used. Earlier such a strategy has been applied for hyper-branched amides [4]. As

TABLE II Thermotropic Mesomorphism of Poly(propylene imine) Dendrimers **4** [2]

Dendrimer	Tg	Cr		Mesophase		Iso
4a (1K1)[a]	–	●	148.5[b]	–		●
4b (1K3)	5	●	45.5[b]	Col$_{rd}$	91.5	●
4c (3K2)	17	●	72.0	Col$_{hd}$	116.0	●
4d (4K1)	21	●	67.0[b]	SmA	{64.5}	●
4e (5K2)	23	–		[Cub]	[~ 50 ± 5][c]	●
0				Col$_{hd}$	96,5[d]	

Tg – glass temperature; Cr – crystal; Iso – isotropic liquid; Col$_{rd}$ – columnar rectangular mesophase of disordered type; Col$_{hd}$ – columnar hexagonal mesophase of disordered type; Cub – optically isotropic cubic mesophase; SmA – smectic A phase.

[a] The first number is a number of generation; K1, K2 or K3 = lateral substituent R (see Fig. 5).

[b] The mesophase exists only at first heating.

[c] The mesophase was not determine by DSC. With the help of polarizing microscopy the decreasing of viscosity as well as of intensity and relaxation time of birefringence induced by the shearing deformation has been observed at ~50 ± 5°C.

[d] The mesophase appears only after a long stay at about 75°C.

{} – liquid crystal phase is observed monotropicaly only at first cycle of heating (that is, it is *pseudoenantiotropic*).

[] – monotropic mesophase in the attitude to Col$_{hd}$ phase, which has been found only at first heating and was not detected by DSC measurements.

a result 100%-protonated analogue **4f** (3-K2·14DSA) displays two types of mesophases in thermotropic state: Mes_1 phase, which appears between 43 and 135,5°C only on first heating, and Mes_2 phase existing between 135,5 and 160°C [5]. The beginning of decomposition without a weight loss was observed at 160°C. The weight loss starts at 190°C on the data of TGA.

Poly(propylene imine) dendrimer of the 4th generation, **4a** (4-K1), displays a *monotropic* mesomorphic state with the respect to the first heating. Consequently, the induction of *enantiotropic* mesophase is easy to prove.

Poly(propylene imine) dendrimer of the 5th generation, **4e** (5-K2), forms a thermotropic mesophase (Col_{hd}) after the annealing at 70°–80°C. Without such annealing, an isotropic cubic phase is found [2]. The transition from an optically isotropic texture to a birefringent one, which appears without any shearing deformation, will be a sign of the induction of a new lyomesophase.

Lytropic Mesomorphism

As to be seen from the Table III, thermotropically *non-mesomorphic* **4a** (1-K1) forms a lyotropic phase in binary mixtures with chloroform, cyclohexane, decanol or ethanol:chloroform (5:1) mixture even at room temperature. In this case we could suggest 2 effects:

- filling in the free volume between the end-group chains at the periphery of the dendrimer molecule by bulky solvent molecules with the increase of microsegregation processes [6];

TABLE III Lyotropic Phase Behaviour Some of Poly(propylene imine) Dendrimers **4** in Binary Systems with Various Solvents, T = 20°C

	Solvents							
Dendrimer	$CHCl_3$	n-hexane	Cyclohexane	Decane	Decanol	$\frac{C_2H_5OH}{CHCl_3}$ (5:1)	THF	DMFA
4a (1-K1)	Lyomes	Cr + Solv	Lyomes	Cr + Solv	Lyomes	Lyomes	Cr + Solv	Cr + Solv
4d (4 K1)	Lyomes	Cr + Solv	Cr + Solv	Cr + Solv	Gel	Cr + Solv	Lyomes	Cr + Solv
4c (3-K2)	Lyomes	Lyomes	Lyomes	Cr + Solv	Lyomes	Cr + Solv	Lyomes	Cr + Solv
4e (5-K2)	Lyomes	Cr + Solv	Lyomes	Cr + Solv	Gel	Cr + Solv	Lyomes	Cr + Solv

Cr = crystalline phase, Lyomes = lyomesophase, Solv = solvent, Gel = gel phase.

- formation of intermolecular H-bonds. It has been shown earlier by means of FTIR- and NMR-spectroscopy that in chloroform the number of H-bonds increases in these systems [2]. First of all, the dendrimers of the 1st and 2nd generation show **inter**molecular H-bonding. However, with higher generations **intra**molecular H-bonding begins to dominate in these dendrimers [2].

As for the induced lyomesophase it was important to know its temperature and concentration range we built the phase diagram of binary system composed of 4a with decanol (Fig. 6). Decanol was chosen due to its high

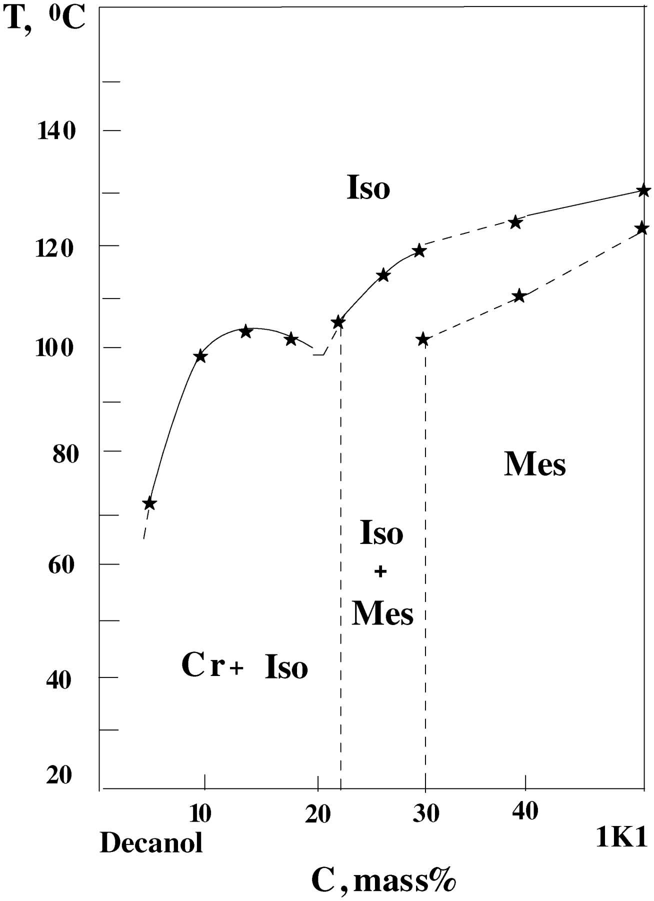


FIGURE 6 The fragment of simplified phase diagram of **4a**(1K1)/decanol binary system, on heating.

boiling point what it convenient for the creation of binary mixtures with exactly known concentration of components. Unfortunately we could achieve the homogeneous samples with the solvent only at the mesogen concentration up to 50 mass % because the increase of mesogen concentration leads to decreasing of miscibility with the solvent. Preliminary heating of the samples with the aim of homogenisation has not been possible, because of thermal instability of system. That is why the phase diagram **4a** with decanol has been obtained only in concentration region from 10 to 50 mass % of mesogen. It shows that lyotropic mesophase with non-geometrical texture could be seen since about 23 mass % of dendrimer (at first, in two-phase region besides to isotropic liquid and then – individually).

Dendrimer **4b** (1K3) displays in binary mixtures with cyclohexane, decane, decanol or DMF, besides thermotropic Col_{rd} mesophase (with grainy texture), two other lyotropic mesophases: viscous mesophase with pseudo-isotropic texture (probably cubic one) and lyomesophase with non-geometrical texture.

As can be seen from the Table III, monotropic **4d** (4-K1) in contact preparations with cyclohexane does not display any inducing effect, whereas with chloroform or THF the *induction of enantiotropic* lyomesophases was found at room temperature. This fact is in good agreement with the data concerning the formation of associates by dendrimers in THF. With the increase of generation, molecular interactions due to **polar** poly (propylene imine) segments become stronger. Although these results are obtained for 2-K2 – 5-K2 dendrimers [2], they are probably equally valid for **4d** (4-K1) dendrimer as well: solvation of THF occurs in the inner polar segment of dendrimer.

While the thermotropic phase of **4c** (3-K2) is usually characterized by a spherulitic texture, in lyotropic system of **4c** with THF only a grainy texture can be observed (similar to that of thermotropic **4e** (5-K2), likewise Col_{hd}). Therefrom, we could deduce that the periphery of the dendrimeric molecule is more completely space-filled. Besides, two types of texture: a focal-conic and a grainy one can be observed in binary system with chloroform.

The phase diagram for the binary system **4c**/decanol (Fig. 7) was obtained in the concentration region from 10 up to 70 mass % of mesogen.

As can be seen from comparison of Figs. 6 and 7, the increase of generation number and branching of end-fragments leads to the replacing of crystal state by a gel one. Besides, the concentration of mesogen for mesophase appearance increases and termostability of mesophase decreases.

For **4e** (5-K2) dendrimer, the lyomesophase appears in binary mixtures with chloroform, cyclohexane or THF without any annealing. The contact preparation of **4e** with chloroform proves the existence of two lyotropic phases with Schlieren and grainy textures (Fig. 8).

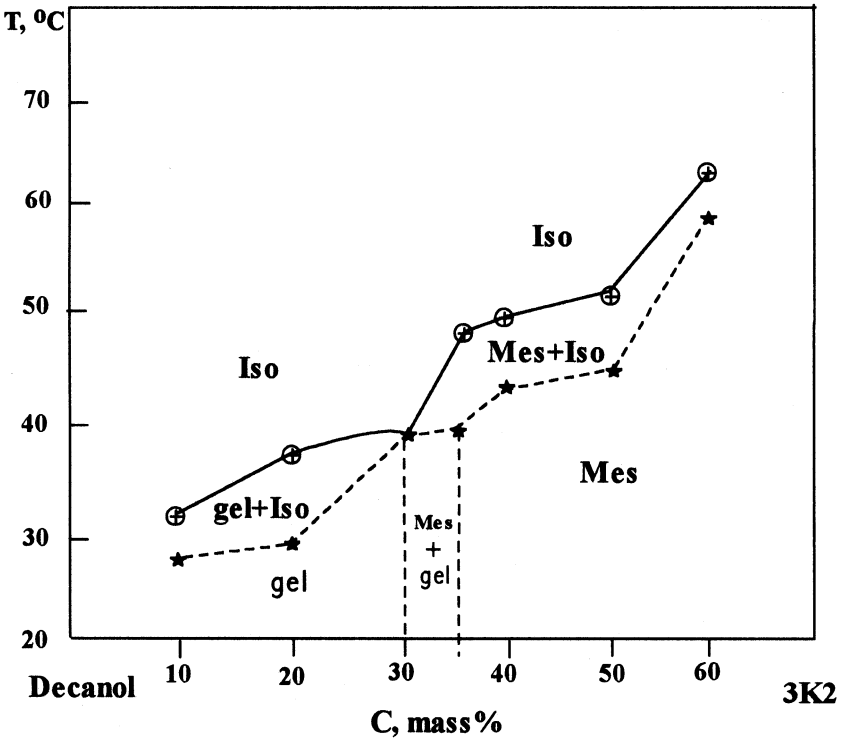


FIGURE 7 The fragment of simplified phase diagram of **4c**(3K2)/decanol binary system, on heating.

The comparative study on lyotropic mesomorphism of protonated dendrimer **4f** (3K2·14DSA) and non-protonated analogue **4c** (3K2) in binary mixtures with solvents of different chemical classes (decane, decanol, cyclohexane, chloroform, THF, DMSO, DMF as well as water and aqueous solutions NaOH and NH_4OH) showed that protonation is favourable not only for thermotropic, but also for lyotropic mesomorphism. For example, in contact preparations with DMSO the non-protonated **4c** (3K2) displays only one lyomesophase with non-geometrical texture, whereas protonated **4f** (3K2·14DSA) shows three type of phases: with non-geometrical, bâttonets/spherulitic textures and viscous isotropic one. In contact preparations with DMF the non-protonated **4c** is non-lyomesomorphic, while the protonated **4f** displays lyotropic polymorphism again. From the textures observed, we presuppose the formation of lamellar (Fig. 9), cubic or new two-dimensional ordered lyomesophases. The detailed study on lyotropic mesomorphism of these mixtures is in progress.

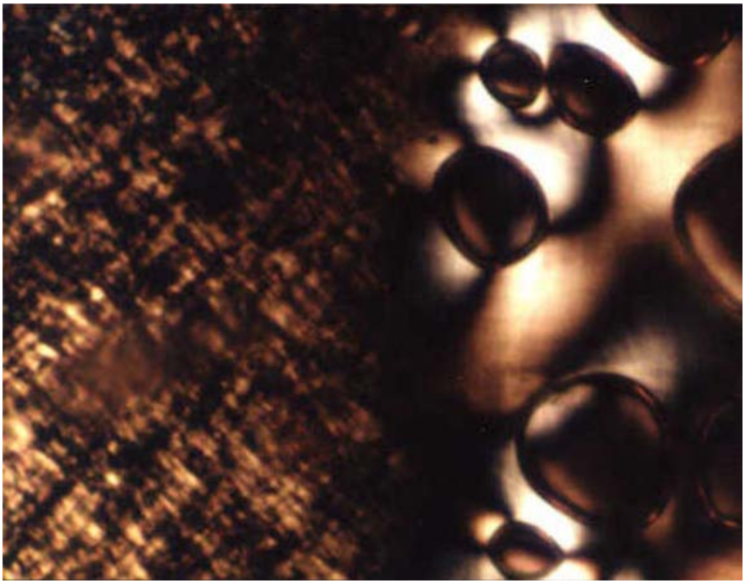


FIGURE 8 Microphotograph of two phases coexistence in contact preparation of **4e** with chloroform at T = 20°C, crossed polarizes, × 250. (See COLOR PLATE III)

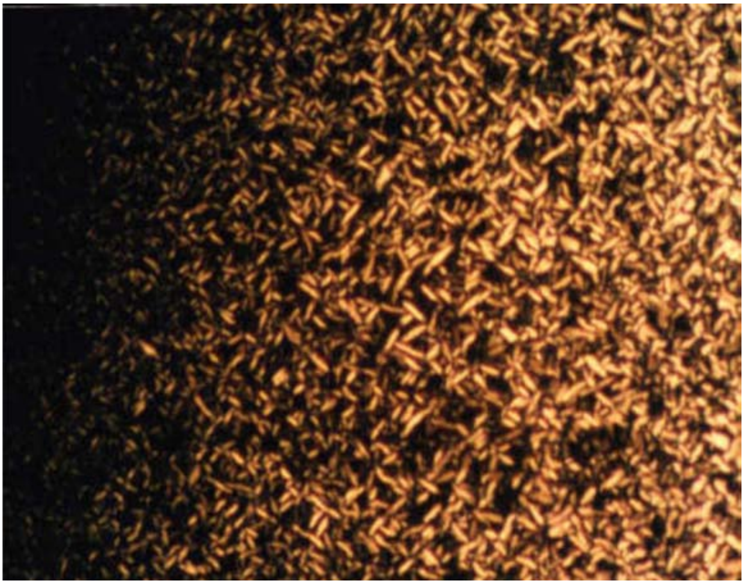


FIGURE 9 Growing bâttonets in **4f**/decanol contact preparation, T = 18,5°C, crossed polarizers, × 250. (See COLOR PLATE IV)

CONCLUSIONS

From the work carried out it has been found that such factors as ***increasing of number of generation***, ***branching of end-groups*** of dendrimers and ***protonation*** lead to stimulation of lyotropic mesomorphism.

The most important results of the influence of *organic solvents* in binary systems with the entitled substances are:

- **induction of a lyomesophase** in the case of non-mesomorphic dendrimer of the first generation **4a** (1-K1);
- **induction of an enantiotropic lyomesophase** in binary system of **monotropic** mesomorphic dendrimer **4d** (4-K1) and triazacyclononane derivative **1d**;
- **lyotropic polymesomorphism** of mesomorphic dendrimers **4d** (4K1), **4c** (3-K2), **4f** (3K2·14DSA) or **4e** (5-K2) as well as triazacylononane derivatives **1c-d**, possessing only one type of thermotropic mesophase;
- **induction of a lyomesophase** in binary systems of thermotropically non-mesomorphic decyloxybenzoyl substituted propylamines **2a-b** or decyloxybenzoyl disubstituted butylendiamine **3b** used as model compounds for studied dendrimers.

Thus, for the first time the induction/variation of mesomorphic properties has been achieved in binary systems of poly(propylene imine) dendrimers as well as with some of their model compounds and 1,4,7-triazacyclononane derivatives with suitable organic solvents.

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