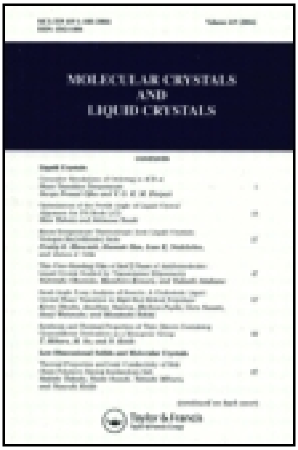

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A Non-Aqueous Lyotropic Liquid Crystal with a Starburst Dendrimer as a Solvent

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A Non-Aqueous Lyotropic Liquid Crystal with a Starburst Dendrimer as a Solvent

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A lamellar liquid crystal was formed by octanoic acid and a starburst polyethyleneimine dendrimer of the third generation:

$$N\{CH_2CH_2N[CH_2CH_2N\{CH_2CH_2NH_2\}_2]_2\}_3$$

The minimum acid content corresponded to an acid/dendrimer molecular ratio of 13, e.g. approximately one acid per amino group. Infrared spectroscopy showed the acid molecules ionized. The maximum number of acids was approximately 2.5 per amino group and now the infrared spectra showed approximately one half of the carboxylic groups to be ionized.

INTRODUCTION

A new class of macromolecules referred to as starburst dendrimers has recently been introduced by The Dow Chemical Company.[1,2,3] They are interesting molecules from the colloid chemical perspective that they are viewed as "covalently fixed" microdomains very reminiscent of spherical micelles.[4,5] The present dendrimers are unimolecular assemblages consisting of concentric tiers (generations) of ethyleneimine (aziridine) segments symmetrically branched through their terminal nitrogens, thus introducing both multiplicity and segment replication (tier to tier) in a geometrically progressive fashion. More recent work by Newkome *et al.*[6a–c] produced cascade molecules which are similar to the starburst dendrimers, however, differ by being more compact and lacking segment replication tier to tier.

The synthesis route to these dendrimers involved exhaustive alkylation of the respective amine terminated generations with N-mesyl aziridine, followed by acid hydrolysis to produce free, deprotected primary amine surface groups as shown in Figure 1.

FIGURE 1

It should be noted that for ideally branched starburst dendrimers in this series, the ratio of tertiary amines: primary amines for generations 1–3 are: (1:3) (4:6) and (10:12), respectively. These ratios are quantized as a function of generation and allow one to establish precise stoichiometry with various reagents. This aspect as well as the dendrimer synthesis will be reported in greater detail elsewhere.

With this communication we introduce the dendrimers into a new role; as the polar solvent in non-aqueous lyotropic liquid crystals. Such liquid crystals were first introduced by Winsor[7] who pointed out that some surfactants such as di-octyl sulfosuccinates (Aerosol OT) in native form exist as liquid crystals. However, his attempts to pre-

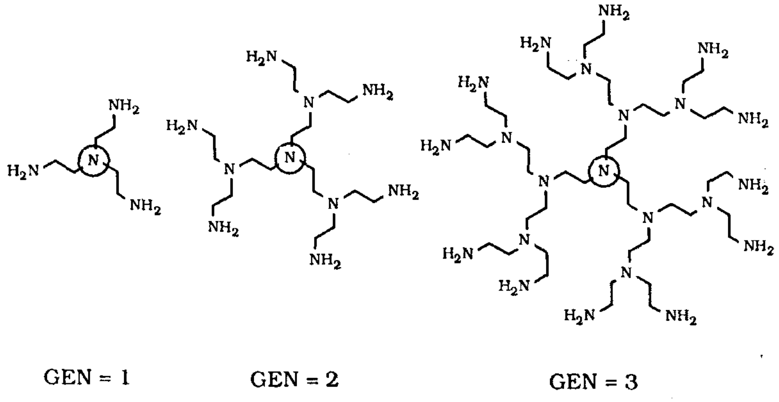

FIGURE 1 Two-dimensional projections of starburst polyethyleneimines (Generations 1, 2 and 3).

pare lyotropic liquid crystals using polar solvents such as ethylene glycol, glycerol, etc. failed[7] and their introduction was delayed for more than 20 years. Moucharafieh[8] first showed in 1979 that lecithin could form lamellar liquid crystals with ethylene glycol. This publication was followed by a series of articles using diols,[9] oligomers of ethylene glycol,[10] ethylnitrate,[11] and glycerol.[12] Attempts to use a polymer met with limited success, however, a polyethylene glycol of molecular weight 515 did lead to a lamellar structure[13] in one instance.

It seemed reasonable to assume that dendritic macromolecules of the type introduced by Tomalia[1-5] should serve as a solvent for non-aqueous lyotropic liquid crystals and with this report we introduce a first example of such a structure.

EXPERIMENTAL

Materials

The octanoic acid was Aldrich Gold Label (>99%) used without further purification. The dendrimers were synthesized according to Tomalia[3] and the water was twice distilled.

Detection of the Liquid Crystalline Phase

The third generation dendrimer, Figure 1, and the acid were mixed in closed vials by repeated centrifugation through a narrow restriction in the center of the vial. The presence of a lamellar liquid crystal was detected by its optical microscopy pattern in polarized light, Figure 2. The phase limit was determined by centrifugation of the mixture at approximately 5000 g for 30 minutes and the phase border calculated from the accounts of the two phases found. Small samples with different initial acid/dendrimer ratios were used to give a reasonable assurance of a correct phase border.

Interlayer Spacing

The interlayer spacing was determined using a Kiessig camera with a Tennelec detector system. Path length was 50 cm and 0.7 mm capillaries with 0.01 mm walls were used.

IR Spectra

The spectra were obtained on a Perkin Elmer IR spectrometer 727B with a scan time of 8 min and a resolution of 3 cm^{-1}. NaCl windows were used and the thickness of the sample was not determined.

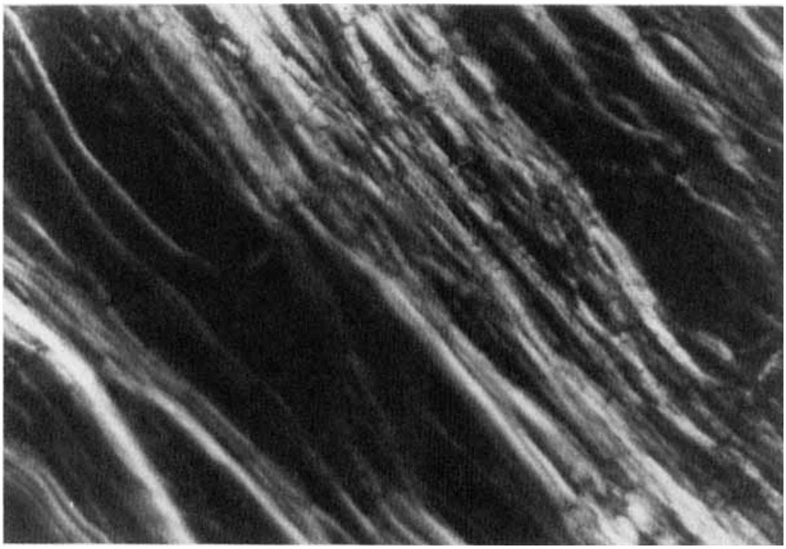

FIGURE 2 The optical pattern is typical of a lamellar liquid crystal.

RESULTS AND DISCUSSION

The lamellar liquid crystal reached from 17.8 to 32.7 by weight of the dendrimer corresponding to acid/dendrimer molecular ratios of 30 to 13. The lowest molecular ratio is close to one acid molecule for each of the twelve primary amino groups of the dendrimer and the IR spectra, Figure 3, showed the antisymmetric stretching absorption 1550 cm^{-1} from the ionized carboxylate group only. The absorption at 1715 cm^{-1} from the acid carboxylic group was insignificant.

For the high acid/polymer ratio the absorption at 1715 cm^{-1} and 1550 cm^{-1} were of similar magnitude, Figure 2, and in addition the IR spectra a weak absorption at 1900 cm^{-1} was found. The out-of-plane bending vibration of the acid *dimers* at 935 cm^{-1} was absent. The weak absorption at 1900 cm^{-1} has earlier been observed[14] in soap acid systems and is characteristic of a carboxylic acid hydrogen bonded to an ionized carboxylate.

The small angle x-ray diffraction pattern gave interlayer distances according to Figure 4. The interlayer spacing was reduced with enhanced amount of solvent, which is contrary to the usual variation.

The results of this investigation deserve comments from two aspects. At first, an explanation is needed of the fact that only the third

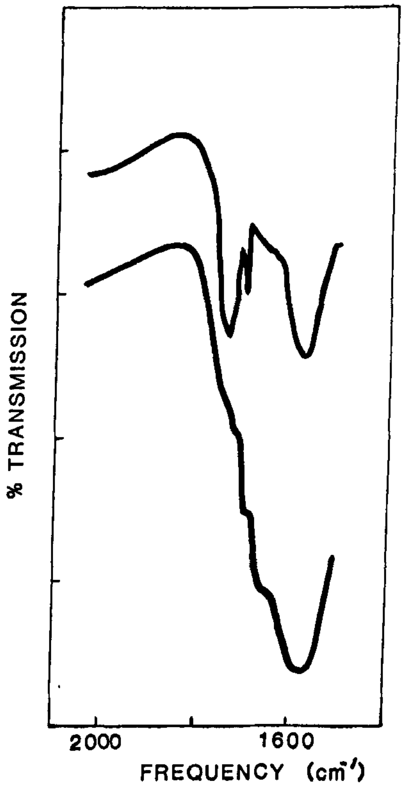

FIGURE 3 Infrared spectra at minimum polymer content (top part) showed the presence of carboxylic acids (1715 cm^{-1}) and ionized carboxylate groups (1550 cm^{-1}). For maximum polymer (lower part) only the latter absorption was found.

generation of the starburst polymers was found to serve as a solvent for a liquid crystalline phase. Secondly, the bonds between the carboxylic groups and the two kinds of nitrogen-based polar groups of the polymer deserve evaluation.

The answer to the first problem appears to reside in the conformation of the polymers. The second generation allows a rich variety of conformations, while third generation is restricted to a disc-shaped form with the terminal amino pairs of the polymer assuming opposite directions to the plane of the disc. The fourth generation, on the other hand, has but little variation of conformations; the overall shape is less of the disc but more of a sphere.

Considering the conformation of the polymer we postulate a liquid crystal structure in which a monomolecular layer of the third gen-

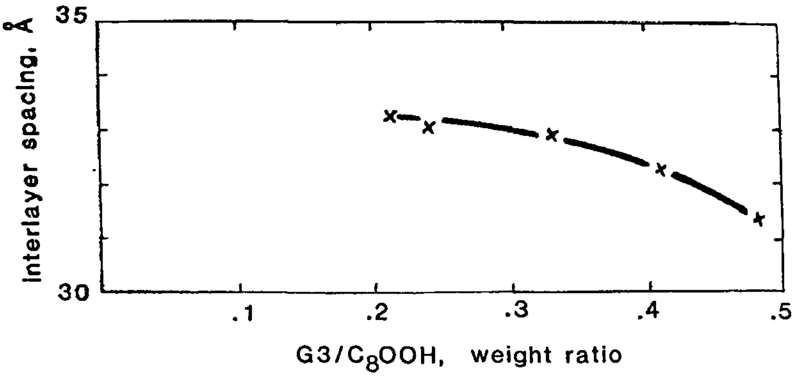

FIGURE 4 Interlayer spacing versus solvent weight ratio. G3 third generation starburst polymer; C_8OOH octanoic acid.

eration polymer forms the solvent layer with the octanoic acid molecules reaching in opposite directions from this layer, Figure 5. Such a structure is consistent with the optical patterns showing a lamellar structure and with the small angle x-ray diffraction data.

The interlayer spacing values, Figure 3, cannot be extrapolated to zero solvent, because of their unusual variation with the solvent content.[15,16] Hence, the contribution from the solvent and amphiphiles must be estimated from the data at the concentration range at which they were measured. The values are in the range 31–33A and an average of 32A is used in the following discussion.

The model for the third generation, Figure 5, gives a thickness of approximately 8A for the disc, leaving 24A for the carboxylic acids. The length of an extended hydrocarbon chain may be estimated at $1.5 + 1.245\,n$, in which n is the number of methylene groups.[17] In the present case two hydrocarbon chains from the octanoic acid each add 10.2A leaving 3.6A to be covered by two layers of carboxylic groups. This value is low considering hydrogen bonded carboxylic groups or ionized ones, but a slightly low value is reasonable because the hydrocarbon chains are probably not fully extended.

Hence, the small angle x-ray diffraction patterns are well within the realm covered by the model, but, of course, provide no proof of it.

The IR spectra provide direct information about the bonds between the carboxylic acids and the nitrogen groups of the polymer. The spectra in Figure 3 show all the carboxylate groups to be ionized at the highest amount of polymer. The molecular ratio acid to polymer is at that point approximately 13. The model suggested for the struc-

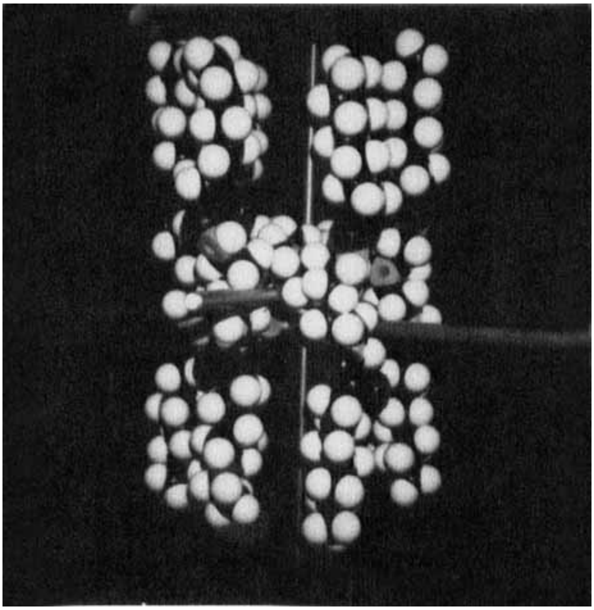

FIGURE 5 CPK model of proposed lamellar liquid crystal assembly of polyethyleneimine dendrimer (Gen. = 3.0) and twelve octanoic acid molecules.

ture proved 6 amino groups on each side of the disc-shaped polymer. The IR spectra are obviously in accord with an organization with 6 carboxylic acids on each side of the disc. All of them are ionized by the amino groups.

At the highest acid/polymer ratio about 30 acids were found per polymer with approximately one-half of them ionized. This result indicates the soap formation to be limited to the amino groups and the interaction between the imine and the carboxylate groups to be restricted to hydrogen bonding.

The bonds for the carboxylic acids, which did not take part in the ammonium soap formation is less obvious. The polar part of the total interactions is reflected to some extent in the infrared spectra, which provide a basis for a preliminary choice between alternatives. Of these the existence of acid dimers may be ruled out; the out-of-plane OH bonding vibration absorbtion at 935 cm^{-1} was completely absent.

The remaining bond sites are also hydrogen bonds; to the imine groups and the ionized carboxylate groups. The tell-tale sign of the latter an absorption at 1900 cm-1 is weak.[14,18] The one found in the present case was extremely weak, Figure 3, and a conclusion of the carboxylic acids forming hydrogen bonds both to the imine groups and to the ionized carboxylic groups seems reasonable.

A detailed description of the structure at the highest acid/polymer ratio must be deferred to a time when more information is available. Suffice it to say that the area of the most extended conformation of the polymer approximates 325A; an area of the order of magnitude necessary to carry 15 acid molecules perpendicularly oriented. Such an arrangement, although possible in principle, does not provide an explanation for the variation of interlayer spacing in Figure 4 and the final description of this structure must await further experimental information.

SUMMARY

A starburst dendrimer of third generation served as solvent in a lamellar liquid crystal. The minimum acid/dendrimer molecular ratio to form the lamellar phase was twelve. In this configuration all the carboxylic acids formed ammonium carboxylates. At the minimum acid/dendrimer ratio approximately one half of the acid formed carboxylate groups; the remaining acids were strongly hydrogen bonded to the carboxylate group.

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