

Photopolymerization of self-organizing ionic liquids†

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In this article we describe the photo-initiated cyclopolymerization of *N,N*-diallyl-*N*-dodecylammonium chloride and *N,N*-diallyl-*N*-hexadecylammonium chloride in aqueous lyotropic mesophases using a low power UVA domestic sunlamp to produce anisotropic polymers. We further demonstrate the formation of cross-linked anisotropic polymer networks upon the addition of 1,8-bis-(*N,N*-diallylammonium)octane chloride.

The search for new environmentally sustainable materials and processing technologies is an often discussed topic in politics and the chemical industry. In particular the replacement of organic solvents in technological processes by solvent-free or water based systems is becoming increasingly desirable. UV-curable polymer systems are therefore of particular interest in the development of new materials. Acrylates and methacrylates are the most popular choice for numerous applications in industry because of their low cost, ease of derivatization and speed of processing. However, the range of UV-curable systems is somewhat limited, so that a larger variety of monomers could extend the range of polymer products with different new and unique properties.¹

Lyotropic liquid crystal polymers are of great interest for the design of new media for reactions or templating as well as in membrane applications *e.g.* gas separation membranes, selective vapour barrier materials, and water nanofiltration and desalination membranes.^{2,3} In this article we demonstrate the potential of diallylammonium salts as alternative UV-curable systems for polymerization in lyotropic liquid crystals to form anisotropic polymers.

Butler and his co-workers reported in the 1950's the polymerization of unconjugated dienes (Fig. 1) and showed that the free radical solution polymerization of diallylammonium salts gave soluble, uncrosslinked polymers with only a very small amount of residual unsaturation. They demonstrated that this polymerization is an intramolecular cyclization

process and, in general, forms linear chains consisting of five- and six-membered heterocycles. The process is best described as an alternating intramolecular cyclization–intermolecular polymerization.^{4–7} The polymers were of considerable industrial importance in ion exchange resins for chromatography and water purification systems.

Hall *et al.*⁸ showed that the photopolymerisation of unconjugated dienes is also an intramolecular cyclization process. Various unconjugated dienes of 5-, 6- and 7-atom center systems (**I** to **III**, Fig. 1) were photopolymerized to give cyclized products and their properties were investigated. The photopolymerization and co-polymerization were carried out in neat or highly concentrated solutions of diallylammonium salt and diallylamide monomers in the presence of commercial photoinitiators to give materials that were suitable for adhesives and coatings.⁹

Hall *et al.* found that in the cases of 7-atom center systems, to which our diallylammonium salts also belong, five-membered rings are formed predominantly, with relatively small proportions of six-membered rings being present (Fig. 2). The formation of a polymer consisting of five-membered rings requires the production of a primary radical intermediate, whereas the generation of six-membered ring systems involves the formation of a more thermodynamically stable secondary radical. In a kinetically controlled polymerization the second process would be disfavored, which is probably the case because of the conformational structure of the intermediate before polymerization.^{10,11} The degree of polymerization is limited due to chain transfer degradation, in which the growing polymer chain is terminated by abstraction of an allylic hydrogen instead of reacting with a monomer vinyl group.

The use of diallylammonium salts as polymerizable groups has some interesting advantages. The price of diallylamine, the precursor to the diallylammonium salts, is low¹² and the compounds are easily functionalized (Fig. 3). The shrinkage in the process of polymerization is low compared to acrylates/methacrylates and the compounds can be handled and transported without autopolymerization. The polymerization is relatively fast, usually around 1–2 minutes.

Although such amphiphilic compounds and their suspension polymerization have been investigated before, neither the

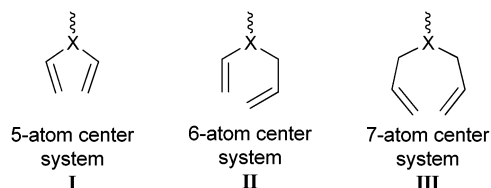


Fig. 1 General structures of starting materials for cyclopolymerization.

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† Electronic supplementary information (ESI) available: Synthesis of **2a–b**, **3a–c**, **4** and **5**. Further POM textures of compound **3a**, **3b**, the mixed system of **3b** and **4**, and the corresponding polymers. See DOI: 10.1039/c0cc01470b

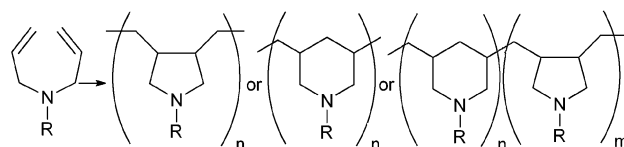


Fig. 2 General reaction scheme of the cyclopolymerization of dienes with 7-atom centers.

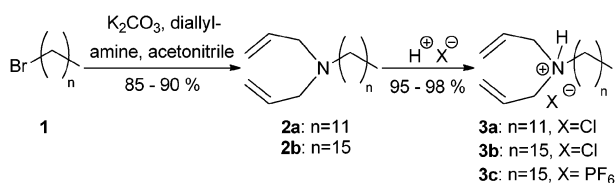


Fig. 3 General reaction scheme for the synthesis of the amphiphiles **3a-c**.

lyotropic phases of the monomers nor the possibility of forming anisotropic polymers by the use of UV polymerisation has been studied.¹³

In order to investigate the properties of the lyotropic phases, we synthesized ionic amphiphiles with the diallylammonium salt as the hydrophilic head group. As shown in Fig. 3, the synthetic route is relatively simple and uses inexpensive starting materials. An alkyl bromide is treated with diallylamine to give the desired diallylaminoalkane **2** in good yield.^{9,14} Compound **2** is readily transformed into the diallylammonium salt **3** simply by stirring with the corresponding acid. Polymerization is carried out in sunlight or by the use of a domestic low-power (75 W) UVA sunlamp and the commercially available photoinitiator 1-hydroxycyclohexylphenyl ketone.

N,N-Diallyl-*N*-dodecylammonium chloride (**3a**) in aqueous media exhibits lyotropic cubic and hexagonal phases. In Fig. 4 the textures observed by polarizing optical microscopy (POM) are shown in a concentration gradient with water. Next to the pure crystal of **3a** a cubic, and at lower concentrations a hexagonal mesophase is formed. After the polymerization the textures of the phases are retained as shown in Fig. 4 (right). A closer look at the lyotropic phases shows that after polymerization the corresponding textures have more grain boundaries. This effect is due to the formation of microdomains during the polymerisation process.

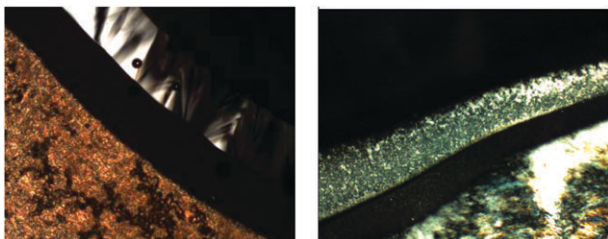


Fig. 4 POM textures of cubic and hexagonal phase of **3a** with water before (left), and after polymerisation at room temperature (right) ($\times 100$).



Fig. 5 POM textures of the lamellar, cubic and hexagonal phase of **3b** with water before (left), and after polymerisation at room temperature (right) ($\times 100$).

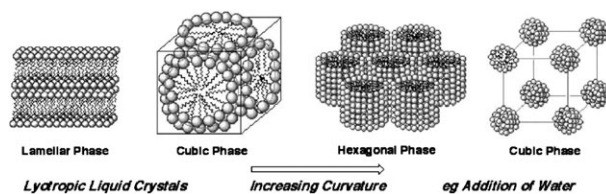


Fig. 6 Schematic structures of the lyotropic mesophases.

In contrast contact preparations of *N,N*-diallyl-*N*-hexadecylammonium chloride (**3b**) with water show, under POM, the formation of lamellar, cubic, and hexagonal phases (Fig. 5, left). These phases were also polymerized under retention of the optical textures (Fig. 5 right). Again, after polymerization grain boundaries can be observed (see also ESI†, Fig. A5).

With increasing water content the curvature becomes larger because more water molecules hydrate the hydrophilic head group. This leads to an overall molecular topology that is more wedge-shaped and eventually leads from the lamellar mesophase to the formation of a bicontinuous cubic phase and to a hexagonal phase (Fig. 6).

It is probable that during the polymerisation in the hexagonal phase the columns are linked at the point where the head groups of one column come into contact with the head groups of neighbouring columns. In the lamellar phase, however, the polymerization cannot take place between layers, which are separated by the aliphatic side chains. Only at defects can the polymerization link the different layers. Therefore we predict that polymerization occurs predominately at the interfaces between layers thereby producing a sheet-like structure.

The lyotropic phase of an amphiphile can often be predicted by using the dimensionless packing parameter S . This simple model takes into account interaction free energies, molecular geometry, and entropy. Thus it is useful in determining the size and shape of amphiphilic aggregates. S is given by $S = V/la$, where V is the hydrocarbon volume, a is the area of head group, and l is the critical length of the hydrocarbon chain.¹⁵⁻¹⁸ The value of S determines the aggregate formed by amphiphiles upon hydration. It has been shown that spherical micelles are formed for $S < 1/3$, hexagonal phases for $1/3 < S < 1/2$, lamellar for $1/2 < S < 1$, and reverse micelles or hexagonal phases for $S > 1$. However, caution has to be taken using this model because the above predicted limits set on the values of S are relatively insensitive to the exact values of V and a , but are strongly dependent upon the choice of l .^{19,20} Applying this model to *N*-hexadecyl-*N,N,N*-trimethylammonium chloride we used: $V = (27.4 + 26.9n) \text{ \AA}^3 = 457.8 \text{ \AA}^3$, where n is the number of carbon atoms in the side chain, $l = 0.8(1.5 + 1.265n) \text{ \AA} = 17.392 \text{ \AA}$.¹⁵ For a , 60 \AA^2 was chosen as this is the value for the cross sectional area of the head group of *N*-dodecyl-*N,N,N*-trimethylammonium chloride at the air/water interface.²¹ This gives for $S = 0.44$ so that a lamellar phase should not be formed. Nevertheless, in the case of **3b** we observe a lamellar phase, so that it can be assumed that the area of the head group must be smaller for **3b**. This can only be the case if the two allyl chains arrange close to each other (Fig. 7, left) instead of a more “spread out” conformation (Fig. 7, right). This conformation is optimal

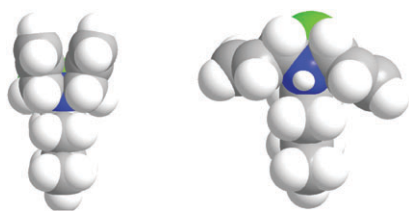


Fig. 7 Side-on view of 3D space-filling models of *N,N*-diallyl-*N*-propylammonium chloride as a representative structure for the conformation of the head group.

for the cyclization reaction during the polymerization process and this might explain the rapid speed of the reaction.

For applications, *e.g.* in membrane technology, polymerization of the cubic phase is of great interest as it is not necessary to align this phase for optimal transport through the membrane in contrast to the hexagonal or lamellar phases. However there are not many polymerizable lyotropic liquid crystalline monomers known that can form and retain cubic phases, and all involve very time or cost-intensive syntheses.^{2,22,23}

In order to cross-link the cubic phase formed of **3b** 9 mol% of 1,8-bis-(*N,N*-diallylammonium)octane chloride (**4**) was added. Compound **4** was synthesized from 1,8-bis-(*N,N*-diallylamino)octane (**5**) by a similar procedure as shown in Fig. 3. Pure **4** does not form a lyotropic phase on the addition of water. However, the homogenous mixture of **3b** and **4** (91 mol% and 9 mol%) formed a lamellar, cubic and hexagonal phase on the addition of water and can be polymerized in these phases (Fig. 8). The cross linked polymer showed high stability and retained the texture even up to around 150 °C, whereas the polymer of pure **3b** started to melt between 80 °C–90 °C (see ESI†, Fig. A7 and A8).

Hall *et al.* found that the water permeability of the polymeric networks of diallylammonium salts strongly depends on the choice of the counteranions.⁸ This property is also reflected by the water solubility of the investigated ionic amphiphiles. While **3a** and **3b** with Cl[−] as the counterion are water soluble and form lyotropic liquid crystals, *N,N*-diallyl-*N*-hexadecylammonium hexafluorophosphate (**3c**) does not form lyotropic phases with water, in fact, the monomer is insoluble at room temperature.

The systems introduced in this communication are very versatile. The material properties can be varied by the choice of bridging group and with the type of counteranion employed. We have successfully polymerized different lyotropic phases and were also able to make cross-linked polymer

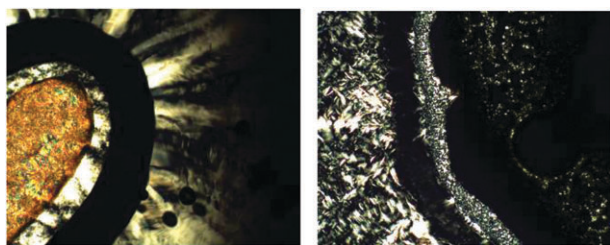


Fig. 8 POM textures of the lamellar, cubic and hexagonal phase of 9 mol% of **4** and 91 mol% **3b** with water before (left), and after polymerization at room temperature (right) ($\times 100$).

networks by addition of a bis-diallylammonium salt. Further research about employing the materials in membranes is in progress.

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Notes and references

- 1 H.-G. Elias, *Macromolecules*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, vol. 2, pp. 289–298.
- 2 M. Summers and J. Eastoe, *Adv. Colloid Interface Sci.*, 2003, **100–102**, 137–152.
- 3 D. L. Gin, J. E. Bara, R. D. Noble and B. J. Elliott, *Macromol. Rapid Commun.*, 2008, **29**, 367–389; D. L. Gin, J. E. Bara, R. D. Noble and B. J. Elliott, *Macromol. Rapid Commun.*, 2008, **29**, 682–683.
- 4 G. B. Butler and F. L. Ingley, *J. Am. Chem. Soc.*, 1951, **73**, 895–896.
- 5 G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, 1957, **79**, 3128–3131.
- 6 G. B. Butler, *Cyclopolymerisation*, in *Encyclopedia of Polymer Science and Engineering*, ed. H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges, Wiley-Interscience, New York, 2nd edn, 1986, vol. 4, pp. 543–598.
- 7 G. B. Butler, *Cyclopolymerisation*, in *Comprehensive Polymer Science*, ed. G. C. Eastman, A. Ledwith, S. Russo and P. Sigwalt, Pergamon Press, Oxford, 1989, vol. 4, pp. 423–451.
- 8 A. W. Hall, K. M. Blackwood, P. E. Y. Milne and J. W. Goodby, *Chem. Commun.*, 2003, 2530–2531.
- 9 (a) A. W. Hall, M. J. Godber, K. M. Blackwood, P. E. Y. Milne and J. W. Goodby, *J. Mater. Chem.*, 2004, **14**, 2593–2602; (b) K. M. Blackwood, P. E. Y. Milne, J. W. Goodby, A. W. Hall and S. M. Kelly, *EP*, 1107997, 2001; K. M. Blackwood, P. E. Y. Milne, J. W. Goodby, A. W. Hall and S. M. Kelly, *GB*, 2354248, 2001; (c) K. M. Blackwood, P. E. Y. Milne, J. W. Goodby and A. W. Hall, *EP*, 1100853, 2001; (d) J. W. Goodby, A. W. Hall, P. E. Y. Milne and K. M. Blackwood, *EP*, 1265942, 2002.
- 10 A. L. J. Beckwith, *Tetrahedron*, 1981, **37**, 3073–3099.
- 11 A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 1985, **41**, 3925–3941.
- 12 Sigma Aldrich online catalogue (13. 04. 2010): 500 ml diallylamine for £30.70; 500 g acrylic acid for £29.30.
- 13 F. Rullens, M. Devillers and A. Laschewsky, *Macromol. Chem. Phys.*, 2004, **205**, 1155–1166.
- 14 Further synthesis of compounds **2a** and **2b**: (a) I. G. Farbenindustrie, *DE*, 681850, 1933; (b) A. R. Katritzky, J. Yao and M. Qi, *J. Org. Chem.*, 1998, **63**, 5232–5234; (c) H. Fuhrmann, I. Grassert, G. Holzhtter, C. Grttnner and G. Oehme, *New J. Chem.*, 2002, **26**, 1675–1681; (d) K. D. Schmitt, *J. Org. Chem.*, 1995, **60**, 5474–5479.
- 15 J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1525–1568.
- 16 J. N. Israelachvili, S. Marcelja and R. G. Horn, *Q. Rev. Biophys.*, 1980, **13**, 121–200.
- 17 J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York, 1985, pp. 229–271.
- 18 C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, Wiley, New York, 1980, pp. 43–59.
- 19 S. Carnie, J. N. Israelachvili and B. A. Pailthorpe, *Biochim. Biophys. Acta, Biomembr.*, 1979, **554**, 340–357.
- 20 R. Nagarajan, *Langmuir*, 2002, **18**, 31–38.
- 21 Q. Zhou and P. Somasundaran, *J. Colloid Interface Sci.*, 2009, **331**, 288–294.
- 22 (a) Y.-S. Lee, J.-Z. Yang, T. M. Sisson, D. A. Frankel, J. T. Gleeson, E. Aksay, S. L. Keller, S. M. Gruner and D. F. O'Brien, *J. Am. Chem. Soc.*, 1995, **117**, 5573–5578; (b) D. Dang, D. F. O'Brien and S. R. Marder, *J. Am. Chem. Soc.*, 2002, **124**, 13388–13389.
- 23 B. A. Pindzola, J. Jin and D. L. Gin, *J. Am. Chem. Soc.*, 2003, **125**, 2940–2949.