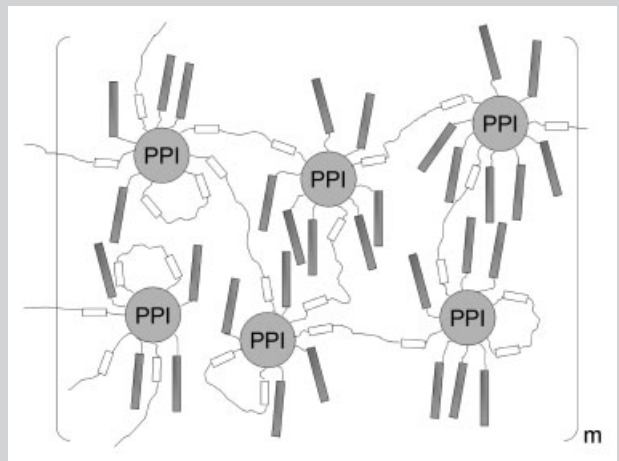


Summary: A nematic liquid crystalline network based on a poly(propylene imine) dendrimer [PPI-(NH₂)₃₂ (G = 4)] was prepared in the form of films. In the network the PPI dendritic molecules are partially functionalised with a chiral aldehyde and are connected to each other by an achiral dialdehyde. The phase behaviour of the network was investigated by polarising-light optical microscopy, differential scanning calorimetry, and X-ray diffractometry. Thermoelastic measurements ruled out the possible elastomeric nature of the material.

Schematic of the nematic dendritic network prepared here.



Liquid Crystalline Dendritic Networks Derived from Poly(propylene imine) (PPI) Dendrimers

Mercedes Marcos,*¹ Rafael Martín-Rapún,¹ José-Luis Serrano,¹ Antoni Sánchez-Ferrer²

¹ Química Orgánica, Facultad de Ciencias-ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

² Albert-Ludwigs-Universität Freiburg Institut für Makromolekulare CHEMIE Stefan-Meier-Str. 31, D-79104 Freiburg, Germany

Received: June 27, 2005; Revised: August 8, 2005; Accepted: August 10, 2005; DOI: 10.1002/marc.200500443

Keywords: dendrimers; liquid crystals; nanostructures; nematic mesophase; networks

Introduction

Dendrimers can be described as well-defined, highly branched molecules that emanate from a central core. As a new class of materials, dendrimers have generated great interest throughout the scientific community. Dendrimers have been widely used as building blocks for the construction of complex supramolecular and macromolecular architectures with precise control of shape and functionality.^[1]

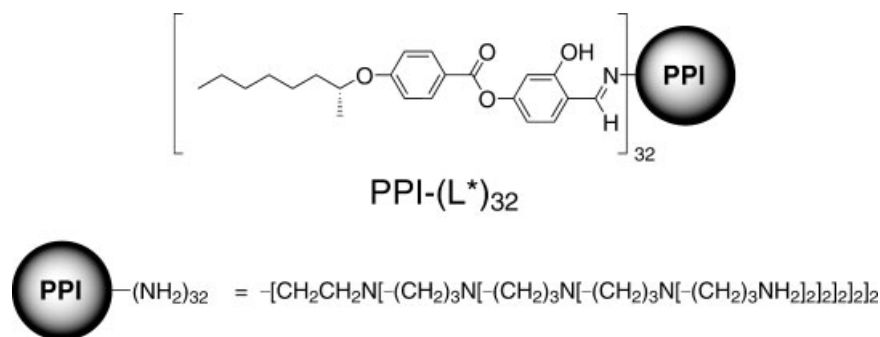
Nowadays, two dendrimer systems are synthesized in large amounts and have become commercially available: they are based on poly(amidoamine) (PAMAM) (Dendritic Nanotechnologies, Inc.)^[2] and poly(propylene imine) (PPI) (DSM).^[3]

A remarkable characteristic of dendrimers is the high concentration of functional groups on their surface. These functional groups can be modified to allow for the design of new materials and the appearance of new properties.^[4] Indeed, for poly(propylene imine) dendrimers, a wide range of modification reactions have been performed^[5] to give rise to new materials such as the so-called “dendritic

box”,^[6] liquid crystals,^[7] dye extraction agents,^[8] chiral dendrimers,^[9] and dendrimers with catalytic sites.^[10]

The functional groups at the surface of the dendrimers can also be used to connect them to each other to prepare supramolecular objects, as was observed in early works in this area.^[2] In this context, Tomalia et al. have coined the term “megamer”,^[11] which stands for an assembly of dendrimers that can be statistic or structure controlled.^[12] At the time that this paper was in preparation, a report was published in which the authors described statistical megamer morphologies and materials obtained from aldehyde-activated generation-4 poly(amidoamine) (G4-PAMAM) and cross-linked G4-PAMAM as building blocks.^[13]

Dendrimers are also of interest in the field of liquid crystals. Indeed, dendritic liquid crystals combine the unique features of low-molecular-weight materials with those of polymers. In this context, we have previously reported the synthesis and characterization of PAMAM and PPI dendrimers in which the mesomorphism can be tuned to exhibit nematic, lamellar, or columnar arrangements depending on



Scheme 1. Schematic representation of the structure of the PPI dendrimer completely functionalised with the chiral monosalicylaldehyde.^[9c]

the structure of the peripherally attached promesogenic units.^[7b]

So far, a variety of mesogens have been connected to a dendrimeric matrix.^[7,14] However, to the best of our knowledge, there is no report concerning liquid crystalline dendritic networks. A dendritic network shall be defined as the deliberate connection, through covalent or non-covalent means, of multiple dendritic units to result in architectures with dimensions greater than those that would be obtained by the preparation of standard dendrimers.^[15] This “deliberate connection” results in at least one fewer degrees of freedom with respect to the relationship of individual dendrimers to other macromolecules in the network. Dendritic networks have applications in diverse

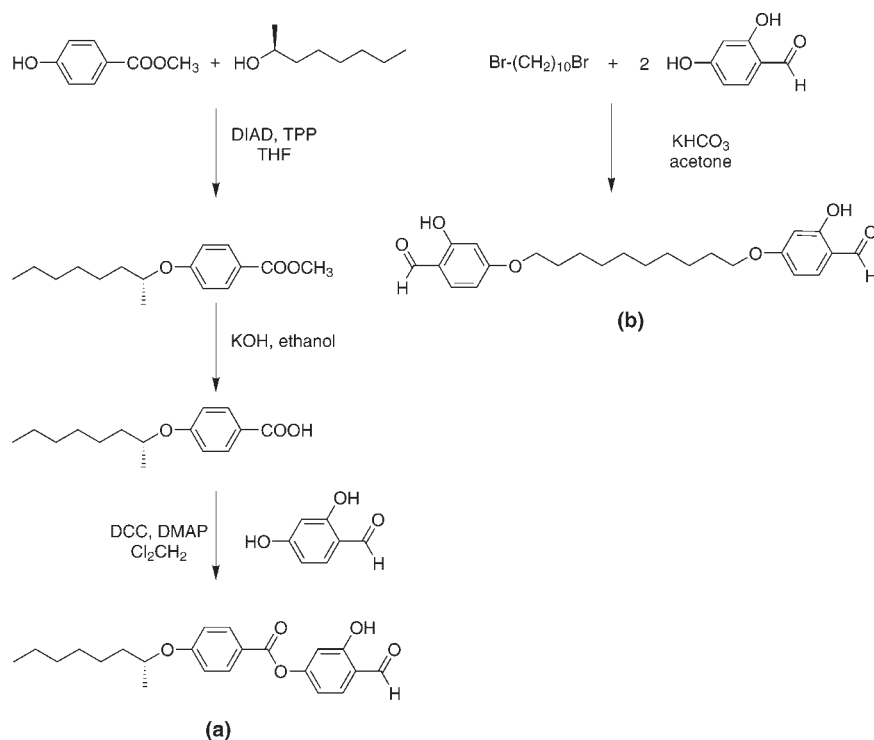
areas of materials science, such as molecular electronics, biomolecular engineering, and (liquid) crystal engineering, to mention just a few.^[15]

We decided to investigate systems containing poly(propylene imine) dendrimers [PPI-(NH₂)₃₂ (G = 4)] with chiral non-mesogenic units connected to each other by dialdehyde moieties to prepare a liquid crystalline dendritic network.

Experimental Part

Chemicals

2,4-Dihydroxybenzaldehyde, 1,10-dibromodecane, (*S*)-2-methylheptan-1-ol, methylhydroxybenzoate, diisopropylazo-



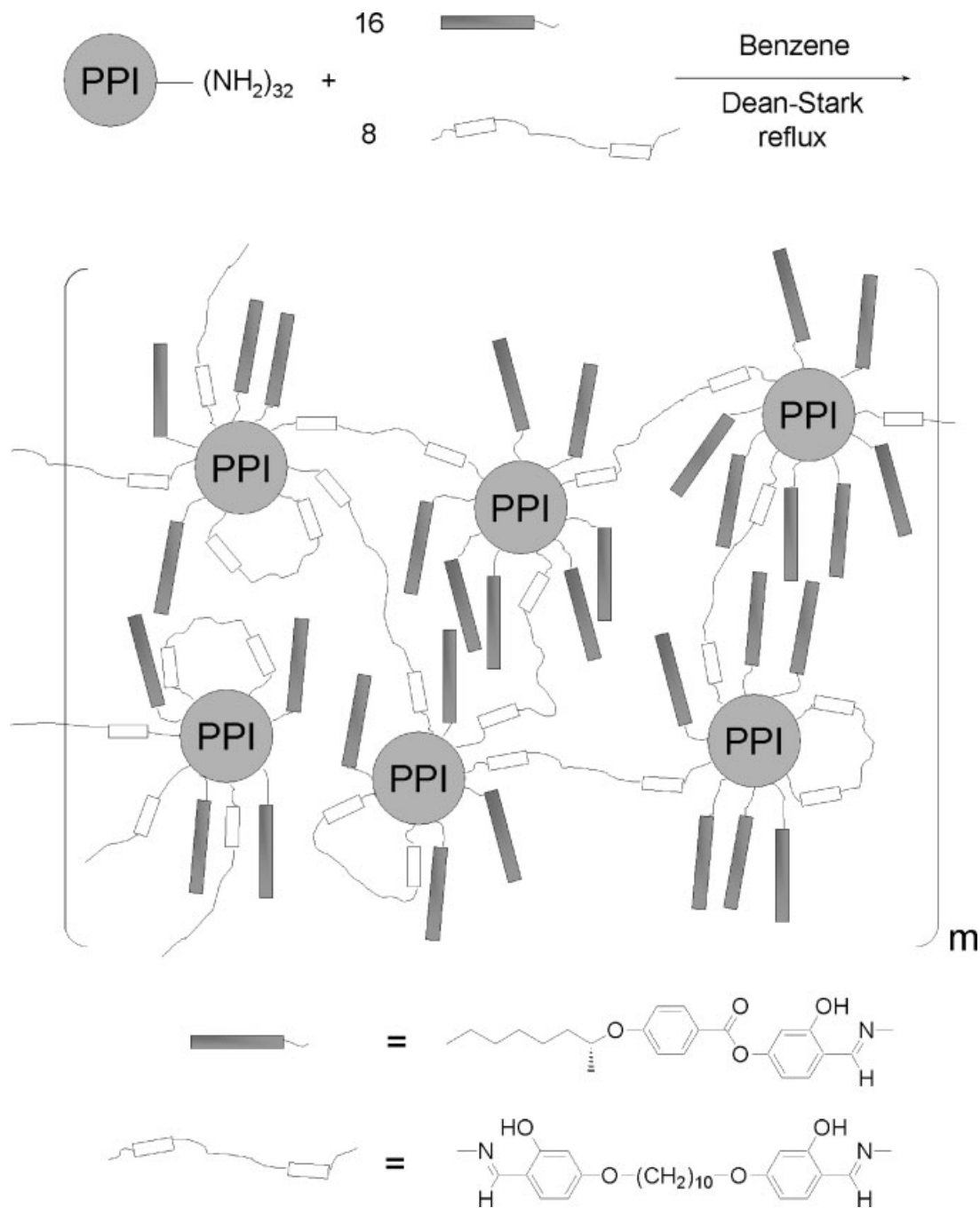
Scheme 2. Synthetic route for the mono- (a) and di- (b) aldehydes.

dicarboxylate (DIAD), triphenylphosphine (TPP), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and poly(propylene imine) dendrimer (PPI-(NH₂)_n) (*n* = 32, *G* = 4) were purchased from Aldrich Chemical Co. All substances were used without further purification.

Benzene was purified by standard methods (refluxed over calcium chloride, distilled, and stored over 4 Å molecular sieves). Dichloromethane was distilled over calcium hydride just prior to use.

Synthesis

The chiral monosalicylaldehyde was synthesized following the method previously reported.^[9c] It was chosen because the dendrimer with which it was completely functionalised, PPI-(L*)₃₂, exhibits no mesogenic behaviour (Scheme 1).^[9c] The bifunctional reactive monomer was synthesized by reaction of the 1,10-dibromodecane with 2,4-dihydroxybenzaldehyde (Scheme 2).^[16]



Scheme 3. Scheme of the preparation of the nematic dendritic network.

The synthesis of the network was carried out as shown in Scheme 3. The general procedure for the condensation of the chiral monosalicylaldehyde and the achiral disalicylaldehyde with poly(propylene imine) PPI-(NH₂)₃₂ (G = 4) was as follows (Scheme 3): To a stirred solution of the mono- and dialdehydes in the appropriate proportions in benzene (20 mL) was added a solution of the equivalent amount of the PPI-(NH₂)₃₂ dendrimer in benzene at 60 °C. The mixture was heated under reflux with a Dean-Stark apparatus until the aldehydes had completely reacted (usually overnight). The solution was evaporated under vacuum and the resulting product was dissolved in dichloromethane and purified by column chromatography using dichloromethane as the eluent. The product-containing fraction of the column was centrifuged to eliminate the remains of the silica gel and was filtered through a millipore filter.

Techniques

Infrared spectra were obtained with a Mattson Genesis II FT-IR spectrophotometer in the 400–4 000 cm⁻¹ spectroscopic range. The optical textures of the mesophases were studied with a Nikon polarising-light optical microscope equipped with a Linkam THMS 600 hot-stage and an Linkam TMS 91 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10 °C · min⁻¹ for heating and cooling. The apparatus was calibrated using indium (156.6 °C; 28.4 J · g⁻¹) as the standard.

The X-ray diffraction (XRD) patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu K α beam. The sample was held in Lindemann glass capillaries (1 mm diameter). The capillary axis was perpendicular to the X-ray beam and the pattern was collected on flat photographic film perpendicular to the X-ray beam.

Results and Discussion

Formation of the Film

The solution in dichloromethane, which was obtained by column chromatography as mentioned above, was concentrated by evaporation under vacuum and deposited on a Teflon substrate. After the slow evaporation of the solvent for 24 h the film was dried under vacuum for 5 h. The films, once formed, were insoluble in common solvents such as methanol, dichloromethane, tetrahydrofuran, acetone, or water.

Initially, Al₂O₃ was used as a drying agent for the synthesis of the network in dichloromethane.^[17] However this method prevented the preparation of pure films because of the encrustation of Al₂O₃ particles into the network. Figure 1 shows a microphotograph of a film prepared using Al₂O₃. Small encrustations of the drying agent can be observed in the film.

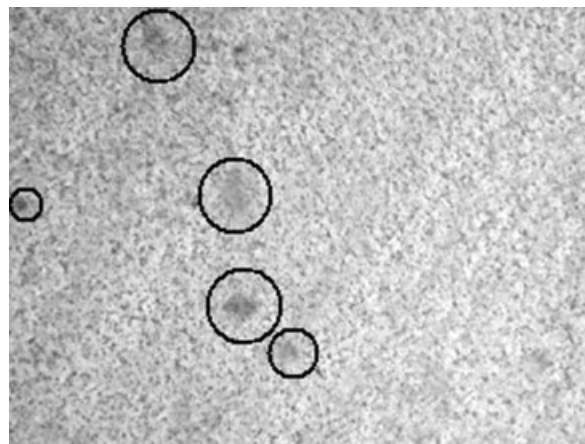


Figure 1. Microphotograph of the network observed under the microscope at room temperature. Small particles can be seen as darker areas. The circles have been traced for an easier detection of the encrustations.

Mesogenic Behaviour

The mesomorphic properties of the materials were investigated by DSC, polarising-light optical microscope (POM), and XRD.

The transition temperatures of the network and its precursors are summarised in Table 1. As can be seen in Table 1, the homodendrimer completely functionalised with the monoaldehyde does not exhibit liquid crystal properties at room temperature. For the network, neither a glass transition nor the clearing point could be detected by DSC, even in the first heating scan. However, the network formed with the dialdehyde exhibits a nematic mesophase from room temperature to approx. 160 °C whereupon the film (yellow in color) becomes red irreversibly. Under POM, the network is strongly birefringent, which is indicative of an anisotropically ordered material. Photomicrographs of the network with crossed polarisers are shown in Figure 2. The mesomorphic properties can be attributed to the formation of the network structure. XRD studies confirmed the nematic nature of the mesophase. Even with the monoaldehyde being chiral, no chirality could be observed by circular dichroism in the mesophase.

Table 1. Thermal properties of the homodendrimer PPI-(L*)₃₂ and the liquid crystalline dendritic network.

Compound	Phase transition temperatures ^{a)}
	°C
PPI-(NH ₂) ₃₂	Isotropic liquid at RT
PPI-(L*) ₃₂	g/38/I
Network	RT N/160 dec.

^{a)} g = glass, N = nematic mesophase, I = isotropic liquid, dec. = decomposition, RT = room temperature.

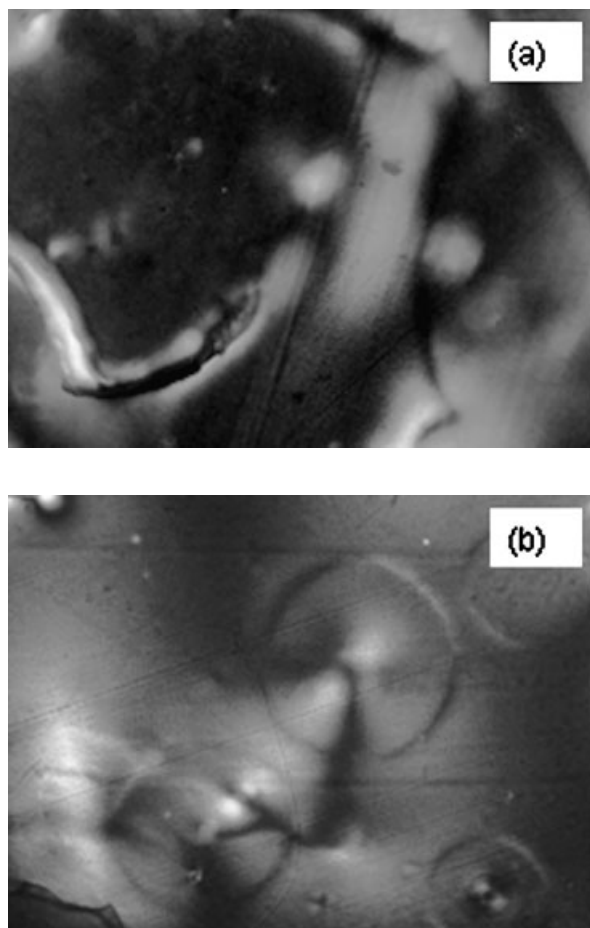


Figure 2. Optical texture of the network observed in the nematic mesophase under the polarising-light microscope at: a) room temperature, b) 81 °C, in the heating process.

An experiment testing the thermoelasticity of the network was performed. The deformation of the material was not reversible.

Conclusion

A nematic liquid crystalline network can be obtained when an amino-dendrimer is added to a solution of mono- and bi-functional non-mesogenic aldehydes. As far as we know, this is the first example of a liquid crystalline nematic dendrimer network described to date. The application of this concept in the preparation of networks may lead to unlimited architectures. A further refinement is certainly needed, presumably by variation of the two main parameters of the network: the monomer reactants (type, length, etc) and the dendrimer (generation, type). Much work is still to be done before finding a good structure that can rival side chain liquid crystalline elastomers.

Acknowledgements: M. M. dedicates this work to the Research Professor of the CSIC, *José Elguero*, to whom she has always looked up and who taught her how to be a universal scientist and an exceptional human being. The authors thank Prof. *Finkelmann* for his suggestions for the preparation of liquid crystalline dendrimers networks. R. M.-R. acknowledges a fellowship from the *Ministerio de Educación y Ciencia*. This work has been supported by the *CICYT* of Spain (MAT 2002-04118-C02-01 and MAT 2003-07806-C01), *FEDER* (EU), and the *Diputación General de Aragón* (Spain).

- [1] [1a] J. M. Fréchet, D. A. Tomalia, "Dendrimers and Other Dendritic Polymers", *Polym. Sci. Ser.*, John Wiley & Sons, New York 1999; [1b] G. R. Newkome, C. N. Moorefield, F. Vögtle, "Dendrimers and Dendrons: Concepts, Synthesis, Applications", Wiley-VCH, Weinheim 2001.
- [2] D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martins, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117.
- [3] [3a] E. Buhleier, W. Wehner, F. Vögtle, *Synthesis* **1978**, 155; [3b] C. Wörner, R. Mülhaupt, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1306; [3c] E. M. M. De Brabander-van den Berg, E. W. Meijer, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1308.
- [4] [4a] P. R. Dvornic, D. A. Tomalia, *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 221; [4b] F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, B. Windisch, *Prog. Polym. Sci.* **2000**, *25*, 987.
- [5] A. P. H. J. Schenning, C. Elissen-Román, J. W. Weener, M. W. P. L. Baars, S. J. van der Gaast, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 8199, and references therein.
- [6] J. F. G. A. Jansen, E. M. M. de Brabander-van den Berg, E. W. Meijer, *Science* **1994**, *266*, 1226.
- [7] [7a] M. W. P. L. Baars, S. H. Söntjens, H. Fischer, H. W. I. Peerlings, E. W. Meijer, *Chem. Eur. J.* **2001**, *7*, 1006; [7b] M. Marcos, A. Omenat, J. L. Serrano, *C. R. Chimie* **2003**, *6*, 947.
- [8] M. W. P. L. Baars, P. E. Froehling, E. W. Meijer, *Chem. Commun.* **1997**, 1959.
- [9] [9a] J. F. G. A. Jansen, H. W. I. Peerlings, E. M. M. de Brabander-Van den Berg, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1206; [9b] J. Issberner, M. Böhme, S. Grimme, M. Nieger, W. Paulus, F. Vögtle, *Tetrahedron: Asymmetry* **1996**, *7*, 2223; [9c] J. L. Serrano, M. Marcos, R. Martín, M. González, J. Barberá, *Chem. Mater.* **2003**, *15*, 3866.
- [10] J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659.
- [11] D. A. Tomalia, S. Uppuluri, D. R. Swanson, J. Li, *Pure Appl. Chem.* **2000**, *72*, 2343.
- [12] [12a] S. Uppuluri, D. R. Swanson, L. T. Piehler, J. Li, G. L. Hagnauer, D. A. Tomalia, *Adv. Mater.* **2000**, *12*, 796; [12b] *Book of Abstracts, 3rd International Dendrimer Symposium*, September 17–20, 2003, Berlin, Germany; [12c] D. A. Tomalia, *Prog. Polym. Sci.* **2005**, *30*, 294.
- [13] A. J. Khopade, H. Möhwald, *Macromol. Rapid Commun.* **2005**, *26*, 445.
- [14] S. A. Ponomarenko, N. I. Boiko, V. P. Shibaev, *Polym. Sci., Ser. C* **2001**, *33*, 1, and references therein.
- [15] G. R. Newkome, C. N. Moorefield, F. Vögtle, "Dendrimers and Dendrons: Concepts, Synthesis, Applications", Wiley-VCH, Weinheim 2001, Ch. 7, pp. 539–562.
- [16] M. Marcos, F. Navarro, L. Oriol, J. L. Serrano, *Makromol. Chem.* **1989**, *190*, 305.
- [17] J. Barberá, M. Marcos, J. L. Serrano, *Chem. Eur. J.* **1999**, *5*, 1834.