Directed Reactions within Confined Reaction Environments: Polyadditions in Polyelectrolyte−Surfactant Complexes

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ABSTRACT: Polyaddition reactions performed within a highly ordered polyelectrolyte−surfactant monomer complex of polydiallyldimethylammonium chloride and di(undecenyl) phosphate give a 1:1 copy of the original lamellar host structure. No phase disruption or disordering occurs during the reaction. The phase morphology of the host before and after swelling and after polymerization is investigated by small-angle-X-ray scattering and transmission electron microscopy. The polymer symplex has an improved thermal and mechanical stability.

Introduction

The formation of polyelectrolyte−surfactant complexes from aqueous solutions of a charged polyelectrolyte and an oppositely charged surfactant has been well studied.[1−4] Substantial efforts have been made to clarify the structure of these highly ordered materials[5−10] with interesting optical,[11,12] biological,[13] and surface energy lowering properties.[14−16] To date, only a few attempts at using polyelectrolyte−surfactant complexes as templates for directed polymerizations have been described in the literature.[17,18]

A template can be defined as a structure-directing agent.[19] In direct templating no change of dimensions or phase transitions occur, and the templated material is a 1:1 copy of the template. This is however complicated by the influence of the growing polymer chain, causing phase disruption and phase separation into a polymer-rich and a template-rich phase. Template polymerization of some monomers in the presence of polyelectrolytes leads to symplexes with more ordered structures than the ones obtained by simple mixing of the two corresponding polyelectrolytes.[20−22] A recent attempt to polymerize surfactant monomers within a polyelectrolyte−surfactant complex by γ-irradiation showed that monomer degradation, rather than initiation of a polymerization reaction within the smectic liquid-crystalline layer, is the preferred reaction pathway.[17] Polymerizations within anisotropic, monomer-swollen polyelectrolyte−surfactant complexes[18] lead to the formation of polymer nanoparticles, which are a colloidal copy of the original template.

Paleos et al.[23] performed an irradiation-induced polymerization on vesicles of the surfactant di(undecenyl) phosphate (ωC11). Here we report the synthesis and characterization of an ordered mesomorphous polyelectrolyte−surfactant complex of this surfactant (ωC11) and polydiallyldimethylammonium chloride (pDADMAC). Furthermore, we describe the use of the complex as a template for the polyaddition reaction of dithiols and the formation of nanostructured polyelectrolyte−polyelectrolyte symplexes.

Thin films of pDADMAC/ωC11 were analyzed by means of small- and wide-angle X-ray scattering (SAXS and WAXS), DMA, TGA, DSC, and TEM. The same analytical techniques were used for the analysis of the complex after the polyaddition of dithiols. Swelling of the organized films with an initiator and two different chain-length dithiols was monitored by the weight uptake of dried films and SAXS analyses.

Experimental Section

Materials. The following chemicals were purchased from Aldrich Co. and used as received: 1,9-nonanedithiol, 1,6-hexanedithiol, 10-undecene-1-ol, phosphorus oxychloride, hexane, high molecular mass polydiallyldimethylammonium chloride (pDADMAC, M_w 375 000−500 000), sodium tetraborate decahydrate, and hydrochloric acid (37%). Water used for the synthesis of the complex was distilled and deionized in a “Milli-Q” water purification system (Millipore Corp.). Azobis(isobutyronitrile) (AIBN) was recrystallized from dry ethanol. Dry benzene (refluxed over calcium chloride, distilled, and stored over molecular sieves 4 Å) was used as solvent for the preparation of ωC11.

Preparation of Surfactant. The surfactant ωC11 was prepared according to a general procedure employed for the synthesis of di(n-alkyl) phosphates.[23] The reaction was carried out by refluxing undecenyl alcohol and phosphorus oxychloride (3:1 molar ratio) in dry benzene for 24 h. Solvent and unreacted alcohol were distilled off under vacuum, and the product precipitated in water. After freeze-drying, white crystals of pure ωC11 were obtained in 60% yield ($T_m = 37-38$ °C).

Complex Preparation. To prepare the complex of pDADMAC/ωC11, the surfactant ωC11 was first dispersed into a buffer of pH 9 (65 mL of 0.1 M Borax mixed with 5 mL of 0.4 M hydrochloric acid) at 65 °C to form a 2 wt % solution of the sodium salt. A 2 wt % aqueous solution of high molecular mass pDADMAC was added dropwise to the surfactant solution in a 1:1 molar ratio. After stirring the solution for 1 h at 65 °C, the precipitated complex was filtered off and washed several times with water to remove salt and excess surfactant. The washing procedure was repeated until no more chloride could be detected with silver nitrate. The complex was dried overnight at 60 °C, followed by drying under vacuum at room temperature for 24 h, and then redissolved in chloroform. The solution was cast, onto Teflon-coated foil. After overnight drying at room temperature the film was further dried at 50 °C and 20 mbar vacuum. All samples were of equivalent thickness, approximately 1 mm.

Polymerization inside the Complex. Films of pDADMAC/ωC11 were weighed, placed in glass bottles, purged for

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10 min with ultrapure nitrogen, and subsequently irradiated, using a γ-ray source and an irradiation dose of 1.66 Mrad.

Polymerization in Bulk. Equimolar amounts of ωC11 and 1,9-nonanedithiol were mixed with 2 mol % AIBN. The reaction mixture was flushed with argon for 5 min and left at 70 °C for 24 h.

Swelling of pDADMAC/ωC11 with 1,6-Hexanedithiol (6SH) and 1,9-Nonanedithiol (9SH). The weighed and dried complex films were swollen by dipping them in a solution of either the 6SH or 9SH (containing 2 mol % AIBN). The film was removed from the solution regularly, excess amounts of dithiol and AIBN were removed, and the film was weighed. The weight uptake was monitored until a 1:1 molar ratio of thiol groups to double bonds was obtained.

Polyaddition Reactions inside the Complex. Swollen films were weighed, placed in glass bottles, flushed with argon for 2 min, sealed, and immersed in an oil bath at 70 °C for 24 h. After polymerization any unreacted dithiol was removed by an overnight Soxhlet extraction of the film with hexane.

Analytical Methods. *Small-Angle X-ray Scattering* (SAXS). SAXS diffractograms were obtained using a standard Kratky camera (Fa. Paar). All swollen films were placed in polymer foil and analyzed under a helium atmosphere to avoid monomer evaporation. Diffractograms of the complex before swelling, after polymerization, and after extraction were recorded under 20 mbar vacuum and at room temperature. The scattering vector s is defined as $s = 2/\lambda \sin\theta$, where 2θ is the angle between incident and scattered light. The measurements were performed in an s range of 1×10^{-2} nm^{-1} < s < 9.0×10^{-1} nm^{-1}.

Wide-Angle X-ray Scattering (WAXS). WAXS diffractograms were obtained on a Nonius PFS120 powder diffractometer in transmission geometry. A FR590 generator was used as a source of Cu Kα radiation.

Elemental Analysis. All measurements were performed on a Fisons elemental analyzer, model 1108. Samples were tested for C, H, N, S, and, in some cases, O content. The commercial pDADMAC used for complex preparation gave some deviations from the theoretical values. On the basis of these new values, the mass percentage of the different elements in the complex was recalculated, and a new prediction for the theoretical values made.

DSC and TGA Analysis. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 200. The samples were examined at a scanning rate of 10 K min^{-1} by applying two heating and one cooling cycle.

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209. The samples were examined at a scanning rate of 20 K min^{-1}.

Transmission Electron Microscopy (TEM). Bright field TEM was performed on a JEM 200CX (JEOL Tokyo, Japan) TEM at an accelerating voltage of 120 kV. Samples of the pDADMAC/ωC11 complex before and after the polyaddition reaction were embedded in epoxy, cured overnight at 60 °C, and stained with OsO_4. Ultrathin sections (~100 nm) were cut from the embedded specimen using a Reichert Ultracut S ultramicrotome and a diamond knife at room temperature. Sections were picked up on 300 mesh copper grids.

Dynamic Mechanical Analysis (DMA). Dynamic mechanical measurements were carried out using a Perkin-Elmer DMA 7e at a heating rate of 5 °C/min and a frequency of 1 Hz. Samples were investigated in the temperature range −130 to 150 °C.

Fourier Transform Infrared Spectroscopy (FTIR). Spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR. A photoacoustic cell was used for the insoluble samples after polyaddition reaction within the complex. The samples were placed in an MTEC 300 chamber and flushed with ultrahigh-purity helium.

Nuclear Magnetic Resonance Spectroscopy (NMR). NMR spectra were recorded on either a 300 MHz Varian VXR spectrometer equipped with a Varian magnet (7.0 T) and a 5 mm switchable probe or a 600 MHz Varian Unity Inova spectrometer equipped with an Oxford magnet (14.09 T) and a 5 mm inverse detection PFG probe. Standard pulse sequences were used for obtaining ^{1}H, ^{13}C, and ^{31}P spectra.

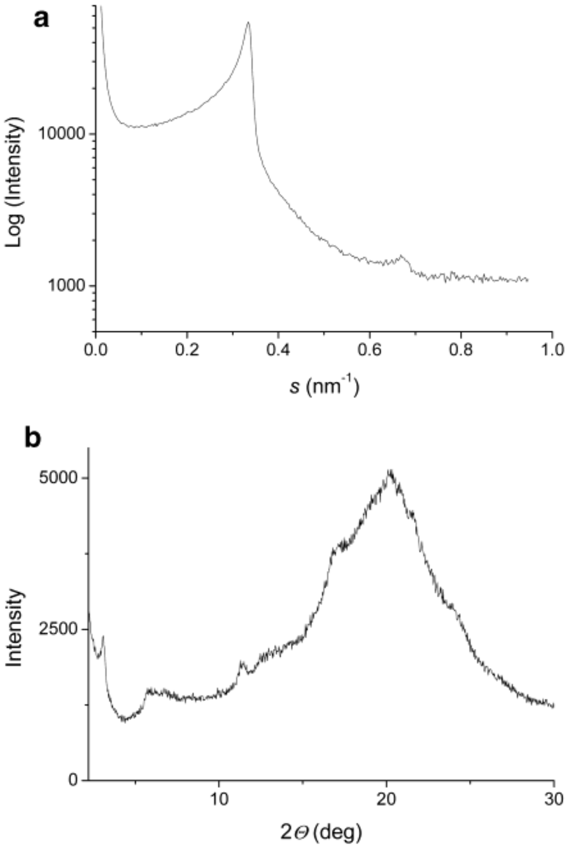

Figure 1. (a) SAXS diffractogram of pDADMAC/ωC11 complex (logarithmic representation). The scattering vector is defined as $s = 2/\lambda \sin \theta$, where 2θ is the scattering angle between incident and scattered light, $\lambda = 0.154$ nm. (b) WAXS diffractogram of the complex.

Results and Discussion

Structure of pDADMAC/ωC11 Complex. Films prepared from PDADMAC/ωC11 were very hygroscopic and deformable. To characterize their thermal behavior, thermogravimetric analysis was performed on the complex. Degradation of the complex occurred above 250 °C (60% weight loss). Elemental analysis showed that a 1:1 stoichiometric ratio of surfactant to polyelectrolyte was obtained. The experimental values were as follows (%, predicted values in parentheses): C, 63.9 (65.5); H, 11.21 (12.2); N, 2.03 (2.02). The 1:1 stoichiometry was also confirmed by ^{31}P NMR spectroscopy, which showed only one peak in the spectra of the surfactant both before and after complexation with a resonance shift of 1.13 ppm.

Strongly birefringent domains could be seen with a polarized light microscope (PLM) without adding mechanical strain to the film. The phase however could not be determined with microscopy as the size of the domains was very small. Differential scanning calorimetry (DSC) showed no detectable phase transition in the temperature range between −50 and 200 °C.

The small-angle X-ray scattering (SAXS) diffractogram of a film of pDADMAC/ωC11 showed a diffraction pattern typical of a lamellar phase. The d spacing of the lamellae was 2.99 nm and corresponds to stretched alkyl chain conformation between the lamellae (Figure 1a). The WAXS analyses showed that the pDADMAC/

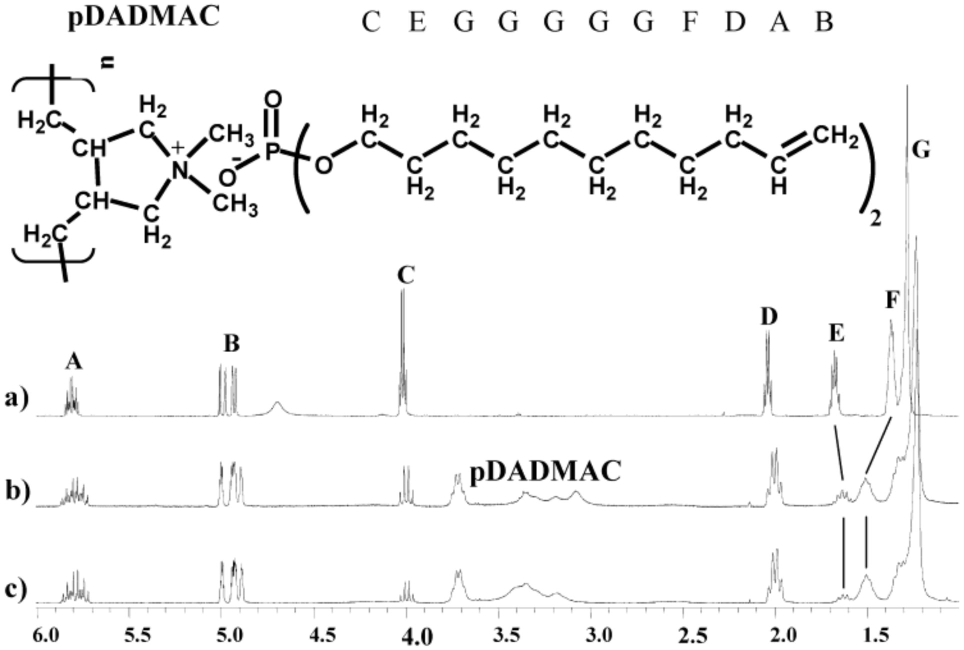

Figure 2. NMR spectra of the (a) surfactant ωC11 and (b) pDADMAC/ωC11 complex before and (c) after irradiation with ^{60}Co source.

ωC11 complex possessed no crystallinity; i.e., the surfactant chains exhibited a liquidlike arrangement. Only a broad halo appeared in the WAXS diffractogram at $2\theta = 20°$ (Figure 1b), which corresponds to a Bragg spacing of 0.44 nm.

Polymerization Reactions: Radiation-Induced Polymerization in pDADMAC/ωC11 Complex. Attempts were made to perform a solid-state, radiation-induced polymerization within the pDADMAC/ωC11 complex, similar to the reaction performed in vesicles of the same surfactant.[23] The results however showed that it was not possible to polymerize the surfactant in the solid complex. No stoichiometric polyectrolyte–polyelectrolyte symplex could be obtained, probably due to the decreased mobility of the surfactant within the complex assembly or a nonappropriate steric arrangement of the double bonds. The ^{1}H NMR spectra of the complex (Figure 2) before and after irradiation were very similar; i.e., the resonances for intact double bonds (indicated by A and B in the figure) were still visible.

Polymerization of Surfactant with 9SH. On the basis of this result, it was clear that a comonomer was needed that would react with the surfactant phase by a free radical mechanism. It is known that thiols add to alkenes or alkynes in the presence of radical initiators.[24,25] Because of the chemical nature of the reactive group of the surfactant, it should therefore be possible to use dithiols to perform a polyaddition reaction inside the complex. This has the advantage (over conventional free radical polymerization) that volume shrinkage is avoided, and the possibilities for phase disruption are minimized.

To ensure that the surfactant reacted with dithiols, equimolar amounts of ωC11 and 9SH were mixed with 2 mol % AIBN and left at 70 °C for 24 h. A white, hard, and brittle solid was obtained after the reaction. The characteristic IR vibrations of the terminal double bond of the surfactant, $\nu_{=C-H}$ at 1095 and 3075 cm^{-1}, $\nu_{C=C}$ 1640 cm^{-1}, and $\delta_{=C-H}$ at 900 and 1000 cm^{-1}, could not be detected in the FTIR spectrum of the polymeric material. The characteristic frequency of the S–H bond, ν_{S-H} in the region between 2550 and 2590 cm^{-1}, was also absent from the IR spectrum. This showed that practically all double bonds and thiol groups had reacted. The newly formed polymer was birefringent under polarized light and therefore anisotropic in nature. This result was confirmed by SAXS analysis of the polymer (Figure 3), which showed that only low order existed. The diffractogram of the polymer showed only broad, low-intensity peaks, from which it was impossible to determine the phase.

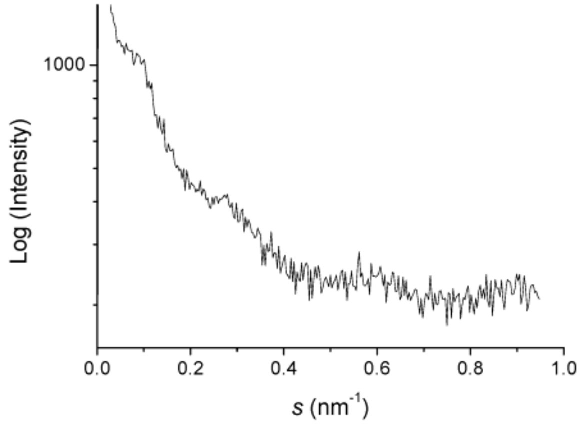

Figure 3. SAXS diffractogram of polymer from the bulk polymerization of 9SH and ωC11.

Polyaddition within the pDADMAC/ωC11 Complex. Swelling of pDADMAC/ωC11 with 6SH and 9SH. Linear swelling behavior was observed during swelling with both thiols. Swelling with 1,6-hexanedithiol proceeded more rapidly.

Films of the pDADMAC/ωC11 complex were swollen to a monomer-to-comonomer molar ratio of 1:1 (approximately 35 wt % for both thiols). After swelling, SAXS characterization of the complex was repeated under a helium atmosphere to ensure no monomer loss through evaporation at reduced pressure. The high order in the complex and the lamellar mesophase was preserved during the swelling experiment, despite the

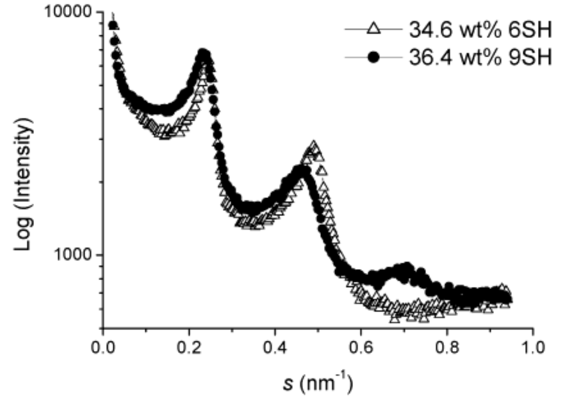

Figure 4. X-ray scattering curves of films of pDADMAC/ωC11 swollen with 6SH and 9SH monomers. Swelling of films with up to 35 wt % of both monomers proceeds without a phase change.

high degree of swelling (Figure 4). The main scattering peak was shifted to smaller scattering vectors (i.e., larger *d* spacings), and a slight broadening of the peaks was observed. In the case of 1,9-nonanedithiol the main scattering peak was found at $s = 0.218\ \text{nm}^{-1}$, corresponding to a repeat unit of 4.59 nm. Two higher-order peaks were also observed at 0.451 and 0.681 nm^{-1}. A peak sequence characteristic for a lamellar phase was found from the diffractogram (ratio 1:2:3). The complex swollen with 1,6-hexanedithiol exhibited a main scattering peak at $s = 0.244\ \text{nm}^{-1}$ (d spacing = 4.10 nm) and one higher order peak at 0.486 nm^{-1}. The peak sequence of 1:2 corresponds to a lamellar mesophase. The material properties of the swollen films were similar to that of the original nonswollen complex; they remained flexible and hygroscopic.

Polyaddition within the Complex. After the polyaddition reaction the films were very hard and brittle and appeared white, compared to the slight yellow color of the soft nonpolymerized complex. It was impossible to dissolve the new material in chloroform (the solvent from which the original films were cast). After a 24 h Soxhlet extraction with hexane (a good solvent for the dithiols) the characteristic thiol smell disappeared from the film. The weight loss after extraction was negligible, indicating that almost all thiol groups had reacted. SAXS diffractograms after the polymerization, both before and after Soxhlet extraction, confirmed that the high order in the complex was preserved. Only a negligible deviation in the positions of the main scattering peak was observed in the complex polymerized with both 9SH and 6SH (Figure 5). WAXS analyses after polymerization with both thiols proved that the complex remained noncrystalline; i.e., the liquid crystalline arrangement of the alkyl tails was preserved during polymerization.

Elemental analysis after extraction of the polymerized films confirmed the ratio of surfactant to dithiol molecules in the complex to be 1:1 (Table 1). DSC showed no detectable phase transitions in the temperature range of −50 to 200 °C, which corresponds to the DSC measurements before polymerization. TGA, however, proved the polymerized samples to be more resistant to temperature than the nonpolymerized complex. The samples lost less than 20 wt % in the temperature range 25−350 °C and only decomposed at around 450 °C. This is a significant increase in thermal stability if compared to the original, nonpolymerized sample. The polymerized complexes were also stiffer than the nonpolymerized one, as found by DMA.

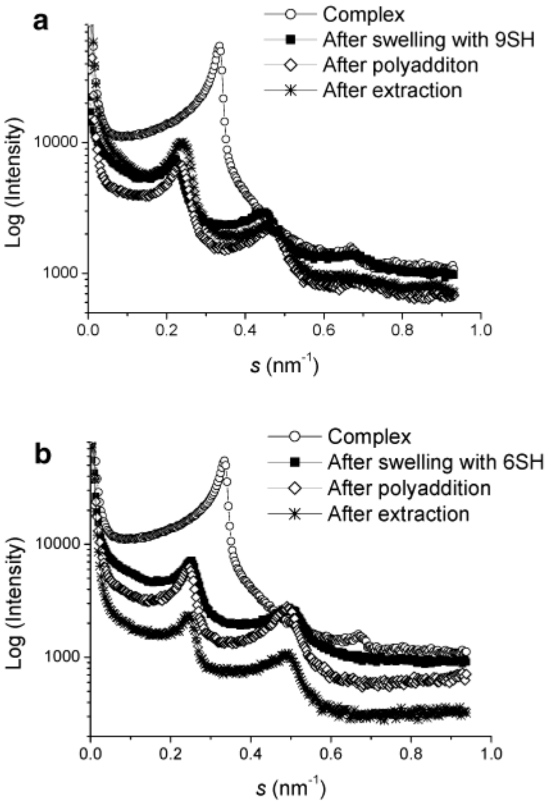

Figure 5. SAXS diffractograms of polyaddition experiments within the pDADMAC/ωC11 complex with (a) 1,9-nonanedithiol (9SH) and (b) 1,6-nonanedithiol (6SH). SAXS measurements were done before and after swelling with dithiol and after polyaddition and extraction of unreacted dithiol.

Table 1. Elemental Analyses of PDADMAC/ωC11 Complex after Polyaddition of Dithiols

complex after addition of	mass percentage experiment (predicted values)			
	C %	H %	N %	S %
6SH	58.99 (60.57)	12.72 (10.78)	1.40 (1.58)	10.69 (9.79)
9SH	62.26 (62.03)	13.21 (10.99)	1.49 (1.49)	8.70 (8.17)

The characteristic IR frequencies of a terminal double bond and that of the S−H group (see above) could not be detected in the IR spectra of the polymerized samples. This provided further proof that there were no reactive groups left in the complex.

The transmission electron micrographs of the complex before and after the polyaddition reaction provided further proof of the existence of a lamellar phase (Figure 6). The micrographs obtained were very similar to recently published data on linear elastomer−amphiphile systems.[26] They showed that continuous copies of the original host structure were formed. The characteristic period increased from approximately 3.0 nm for the nonpolymerized complex to 4.1 nm for the 6SH-polymerized and 4.3 nm for the 9SH-polymerized complexes. These results were in excellent agreement with SAXS data, where the main scattering vector was observed at repeat units of 4.10 and 4.16 nm after the extraction of unreacted dithiol from the complex polymerized with 6SH and 9SH, respectively.

Conclusions

It was shown that the complexation of pDADMAC and ωC11 produces an ordered material with a lamellar

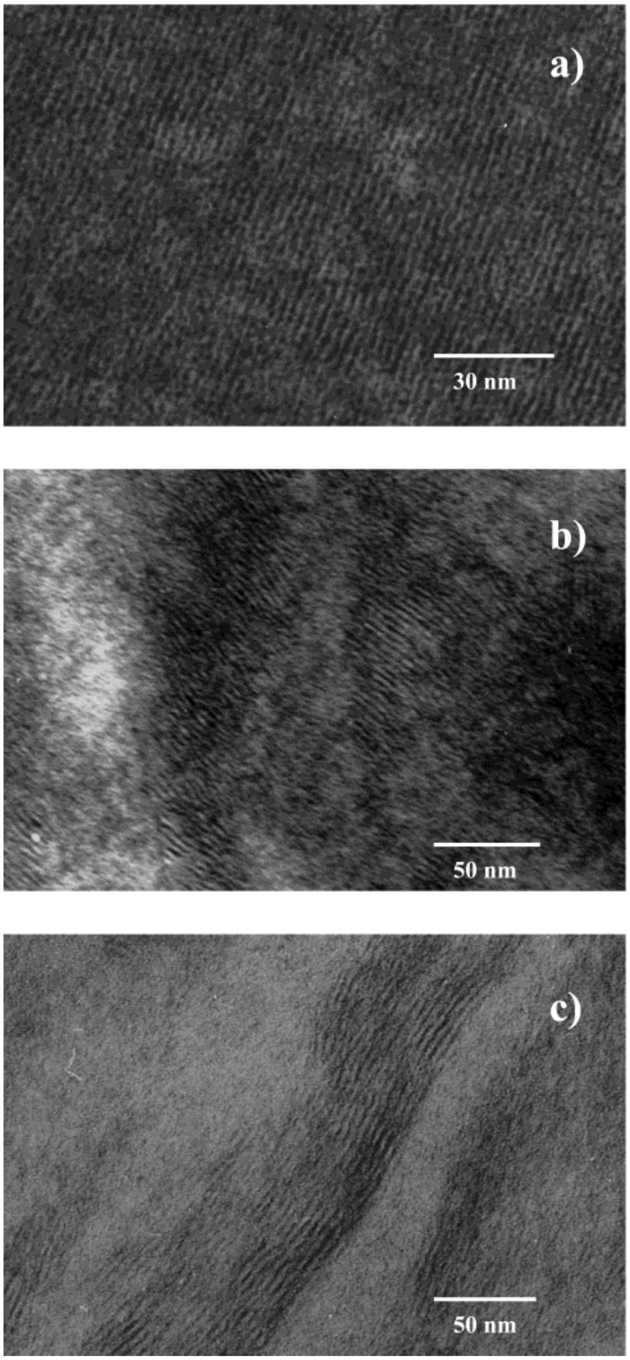

Figure 6. TEM micrographs illustrating the lamellar structure in pDADMAC/ωC11 complex (a) before and after the polyaddition of (b) 6SH and (c) 9SH.

mesomorphous structure. The structure is stable to swelling with more than 35 wt % dithiol. Polyaddition reactions within the complex lead to the formation of a 1:1 copy of the template with no phase disruption or disordering occurring during the reaction. These results were confirmed by both SAXS and TEM. The polymer symplex thus obtained preserves all the typical features of the template. Furthermore, its thermal stability and mechanical properties have improved substantially.

Further investigations will include variations of parameters such as the hydrocarbon volume of the dithiol and the type of polyelectrolyte used on the properties of the resulting polymer.

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