Self-Organized Thermosets: Blends of Hexamethyltetramine Cured Novolac with Poly(2-vinylpyridine)-*block*-poly(isoprene)

Harri Kosonen,[†] Janne Ruokolainen,[†,‡] Per Nyholm,[§] and Olli Ikkala*[,†]

Department of Engineering Physics and Mathematics, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Espoo, Finland; Institute of Biotechnology, Electron Microscopy, University of Helsinki, P.O. Box 56, FIN-00014 Helsinki, Finland; and Neste Chemicals Ltd., P.O. Box 310, FIN-06101 Porvoo, Finland

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ABSTRACT: We demonstrate a concept to prepare thermally cross-linked nanostructured phenolic resins based on self-organization. Novolac, containing hexamethyltetramine (HMTA) as a curing agent, is blended with poly(2-vinylpyridine)-*block*-poly(isoprene), P2VP-*block*-PI, where the block length of P2VP has been selected to be sufficiently high to allow the mutually hydrogen-bonded novolac and P2VP, including HMTA, to be contained in the same microphase-separated domains. The novolac-containing domains have subsequently been cross-linked by thermal curing. By tailoring the block lengths, we demonstrate lamellar, cylindrical, and spherical cross-linked phases using transmission electron microscopy. The concept opens simple schemes to modify properties of common phenolic thermosets.

Introduction

It was suggested by de Gennes that polymer networks with unusual properties could be obtained if cross-linkable polymers were dissolved in for example lipid/water or other liquid crystalline solvents, followed by cross-linking in the ordered state.[1,2] Such considerations, as well as efforts to achieve molecular level reinforcement and tailored properties, have encouraged to combine mesogenic (rigid) moieties and networks, leading to liquid crystalline thermosets and elastomers.[3−6] On the other hand, self-organized nanostructures of various block copolymer architectures have much been pursued.[7,8] There, the structure formation takes place without mesogens, based on the repulsion between the covalently bonded blocks,[9] typically leading to spherical, cylindrical, lamellar, and gyroid phases. More recently, self-organized nanostructures have been constructed on the basis of ionic interactions,[10] coordination bonds,[11] and hydrogen bonds[12−14] between the repulsive blocks, allowing also hierarchical order and functional materials.[15,16] In the latter concepts, the self-organizing entities can be regarded as supramolecules[17] as they are formed due to matching physical interactions.

Blends of thermoplastic homopolymers and block copolymers can also form nanoscale structures. In blends of homopolymer A and block copolymer A-*block*-B, there is an interplay between a macrophase separation and the microphase separation within the block copolymer.[8,18] Homopolymers of sufficiently low molecular weight can be incorporated within microphase-separated domains. Increased molecular weight of the homopolymer leads to a tendency to segregate to the centra of the microphase-separated domains. Finally, when the molecular weight of homopolymer is substantially greater than that a corresponding block of the block copolymer, macrophase separation predominates.[8] In a more general case, phase behavior of a blend consisting of homopolymer C and block copolymer A-*block*-B reminds that of the homopolymer A and block copolymer A-*block*-B when the Flory−Huggins interaction parameter χ_{AC} is much smaller than χ_{AB} and χ_{BC}.[8]

Cross-linking within the self-organized phase poses considerable difficulties, as the energies involved in the chemical reactions may be larger than the weak physical energies involved in the microphase separation. Polymerization in specific surfactant assemblies has been reported.[19−22]

Phenolics belong to the most common thermosets.[23] Lamellar mesophase has been recently demonstrated by polymerizing phenol−formaldehyde in the presence of cationic surfactants.[24] In this work, we use polymeric surfactants, i.e., block copolymers, to demonstrate a general concept to provide common self-organized phases for phenolic resins, i.e., the lamellar, cylindrical, and spherical phases. Novolac, being a hydrogen-bonding donor, is reported to be miscible with several polymers containing hydrogen-bonding acceptors, such as poly(ethylene oxide) (PEO), poly(ϵ-caprolactone), and poly(methyl meth acrylate).[25−28] For example, hexamethyltetramine (HMTA) cured novolac is essentially miscible with poly(ethylene oxide), taken that the weight fraction of PEO before curing is sufficiently small in comparison to that of novolac.[28] In this work, we prepare blends of HMTA containing novolac with poly(2-vinylpyridine)-*block*-poly(isoprene), i.e., P2VP-*block*-PI. Before the cross-linking, one expects that novolac will be incorporated within the P2VP domains due to the hydrogen bonds, taken the novolac molecular weight is sufficiently small. Heat treatment causes cross-linking within the self-organized structures due to the HMTA.

Experimental Section

Materials. Two poly(2-vinylpyridine)-*block*-poly(isoprene) diblock copolymers were provided by Polymer Source Ltd. and were used without further purification. Molecular weights of blocks and polydispersities are shown in Table 1. Novolac was supplied by Bayer Ltd. (Vulcadur A) and was used without further purification. The molecular weight of novolac was about 2000 g/mol. Vulcadur A contains a cross-linking agent

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[†] Helsinki University of Technology.
[‡] Helsinki University, Electron Microscopy.
[§] Neste Chemicals Ltd.

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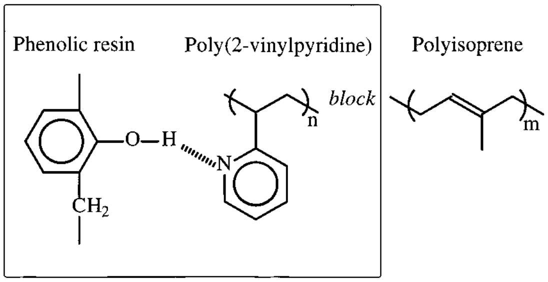

Figure 1. Novolac, P2VP-*block*-PI, and schematics of their mutual hydrogen bonding. Before cross-linking, the blend self-organizes, and in this case the polar domains consist of novolac, P2VP, and HMTA and the nonpolar domains consist of PI. During a thermal treatment, HMTA causes cross-linking of novolac within the polar domains.

Table 1

	$M_{n,P2VP}$	$M_{n,PI}$	M_w/M_n
P1172-I2VP	2800	30 000	1.06
P1168-I2VP	21 000	71 000	1.04

hexamethyltetramine (HMTA, 10 wt %). Tetrahydrofuran (THF) was provided by Riedel-de Häen (99.9%).

Sample Preparation. In the following, the net compositions will be described by the following three interrelated parameters: the total molecular weight of the block copolymer ($M_{n,P2VP-PI}$), the weight fraction of its P2VP block (f_{P2VP}), and the weight fraction of PI in the final blend (w_{PI}). Samples were prepared only using a minor amount of PI, i.e., $w_{PI} = 0.05$, 0.10, 0.15, 0.20, 0.30, and 0.40, as our interest was to modify the structure of novolac.

Novolac (containing HMTA) and P2VP-*block*-PI were added into THF. The mixtures were stirred for 1 day at room temperature and finally for 30 min at 60 °C, followed by evaporation of THF at 60 °C. Samples were subsequently dried in a vacuum oven (ca. 10^{-2} mbar) at 60 °C for 10 min. Curing of the samples was performed in a compression press using pressure 7 MPa at 100 °C for 2 h, at 150 °C for 1 h, and finally at 190 °C for 30 min.

Transmission Electron Microscopy. Bulk samples of cross-linked novolac blends with P2VP-*block*-PI for TEM were imbedded in epoxy and cured at 60 °C overnight. Thin sections (50−100 nm) were cut from the embedded specimen using Leica Ultracut UCT ultramicrotome and a diamond knife at room temperature. To enhance the contrast between the different domains, the microtomed sections were stained in a vapor of OsO_4 crystals. Bright field TEM was performed using a JEOL-1200EX transmission electron microscope with tungsten filament operating at an accelerating voltage of 60 kV.

Results and Discussion

The aim of this work was to achieve self-organized structures of HMTA cured novolac by blending with suitable amphiphilic molecules, i.e., block copolymers. A critical issue is that one block of the amphiphilic molecule has to be sufficiently compatible with novolac whereas the other block of the amphiphilic molecule has to be sufficiently repulsive. After experimenting with various types of potential amphiphilic oligomers and polymers, P2VP-*block*-PI turned out feasible as it is well-known from FT-IR studies that hydroxyl groups form relatively strong hydrogen bonds with poly(vinylpyridine)s.[12,13,29,30] Therefore, it is to be expected that such a hydrogen bonding takes place also in this case. Accordingly, as shown in Figure 1, blends of novolac and P2VP-*block*-PI were expected to form self-organized structures, where hydrogen bonds between the hydroxyl groups of novolac and the nitrogens of P2VP cause selective solubility of novolac within the P2VP domains. PI is nonpolar, and therefore, it microphase separates from the P2VP-, novolac-, and HMTA-containing domains.

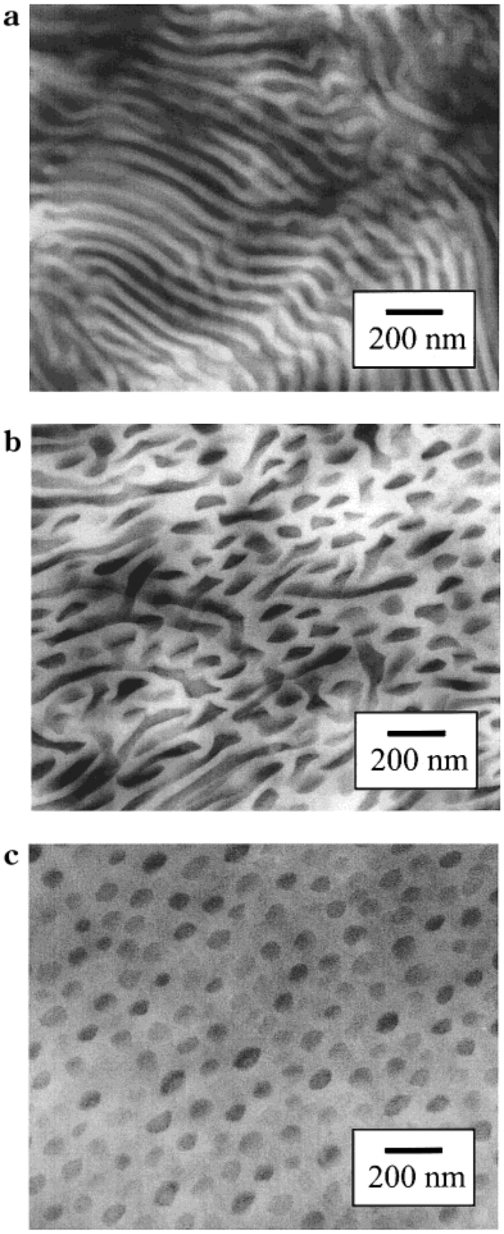

Figure 2. TEM images of HMTA cured blends of novolac and P2VP-*block*-PI where the latter one has the molecular weight $M_{n,P2VP-PI} = 92\ 000$ g/mol. The molecular weight of the P2VP block is $M_{n,P2VP} = 21\ 000$ g/mol, which is much larger than the molecular weight of novolac before cross-linking, i.e., $M_{novolac} = 2000$ g/mol. Weight fraction of PI is (a) $w_{PI} = 0.40$, (b) $w_{PI} = 0.30$, and (c) $w_{PI} = 0.20$ of the total blend weight. The nonpolar PI phase shows black in images due to OsO_4 staining.

However, to achieve such an effect, the molecular weights have to be matched: In the case of thermoplastic polymers, when the molecular weight of a homopolymer C is much smaller than that of the compatible block A of a block copolymer A-*block*-B (i.e., $\alpha = M_{n,C}/M_{n,A} \ll 1$), the homopolymer causes swelling of the corresponding block of the block copolymer and can thus essentially be incorporated within the microphase-separated domains. Our hypothesis was that essentially an analogical result could be observed even if C would be cross-linked. Figure 2a−c describes first a case where P2VP-

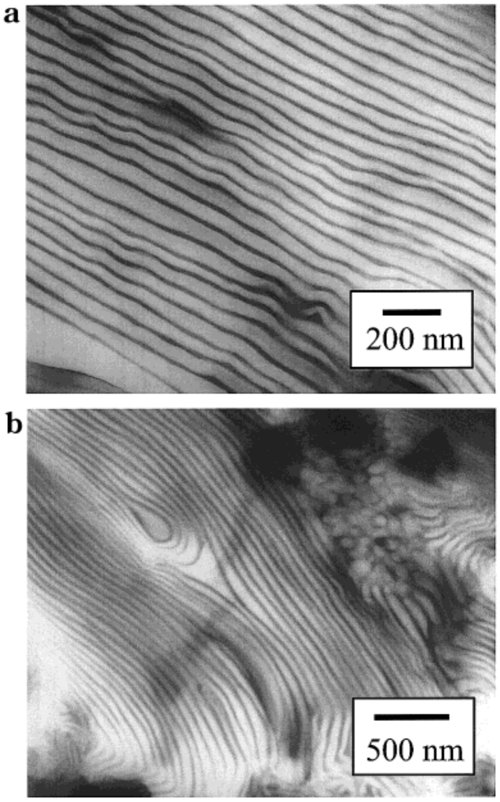

Figure 3. TEM images of HMTA cured blends of novolac and P2VP-*block*-PI where the latter one has the molecular weight $M_{n,P2VP-PI}$ = 32 800 g/mol. The molecular weight of the P2VP block is $M_{n,P2VP}$ = 2800 g/mol, which is only slightly larger than that of novolac before cross-linking $M_{novolac}$ = 2000 g/mol. Weight fraction of PI is (a) $w_{PI} = 0.40$ and (b) $w_{PI} = 0.20$ of the total blend weight. The nonpolar PI phase shows black in images due to OsO_4 staining.

block-PI has a molecular weight $M_{n,P2VP-PI}$ = 92 000 g/mol and the weight fraction of its P2VP block is $f_{P2VP} = 0.23$, and the structures have been thermally cross-linked at the end. In this case, the P2VP blocks have molecular weights of 21 000 g/mol whereas the novolac chains with 2000 g/mol are short in comparison to the P2VP blocks, leading to a small value $\alpha = M_{novolac}/M_{n,P2VP} = 0.095 \ll 1$. Figure 2a shows a lamellar self-organized structure that is achieved when the weight fraction of poly(isoprene) is 40 wt % of the total weight of the blend ($w_{PI} = 0.40$). A long period of this structure is ca. 700 Å, and the thickness of PI phase, shown black in images, is of the order of 300 Å. Relatively well-ordered structure is observed which may be due to the high fraction of un-cross-linked poly(isoprene) and the effect of annealing that may have taken place upon curing at the elevated temperature. Figure 2b shows the case where the weight fraction of poly(isoprene) has been reduced to $w_{PI} = 0.30$. In this case less well-defined structure is observed, consisting of wormlike elongated objects. The structure of Figure 2b may be assigned as a relatively poorly ordered cylindrical phase. Finally, Figure 2c shows a spherical self-organization with a further reduced weight fraction of poly(isoprene), i.e., $w_{PI} = 0.20$. The size of spheres and their average distance were ca. 600 Å and ca. 1200 Å. The structures of Figure 2 roughly agree with those expected for un-cross-linked diblock copolymers and blends of homopolymer A and diblock copolymer A-*block*-B in a strong segregation limit.[8] The self-organized structures were not perfectly ordered obviously because the samples could not be annealed before the cross-linking took place. Therefore, only a flat intensity maximum was seen using small-angle X-ray scattering. SAXS curves are not shown here, but long periods obtained with SAXS were of the same order than those observed using TEM.

Figure 3 describes the corresponding case where the length of the P2VP block has been reduced to 2800 g/mol, which is essentially the same as that of novolac prior cross-linking, i.e., 2000 g/mol. In this case, there is a tendency to expel the novolac chains to the center of the microphase-separated P2VP domains. As can be seen from Figure 3a, a lamellar organization takes place for $w_{PI} = 0.40$. However, a combination of lamellar and inverse cylindrical nanostructures seem to form when $w_{PI} = 0.20$ (see Figure 3b). Surprisingly, the long periods of nanostructures of Figure 3a,b (about 550 Å) did not essentially change when the weight fraction of PI was reduced. Thickness of black PI phase was ca. 200 Å, which is smaller that in Figure 2a, as it should be, because the molecular weight of PI block is reduced.

At the proof stage we became aware of related studies concerning amine cured epoxies which render self-organized thermosets upon blending with block copolymers.[31,32]

Conclusion

Cross-linked systems are often more stable under chemical and physical conditions than the linear polymers. It is therefore desirable to develop concepts to tailor their properties, and nanostructuring of cross-linked thermosets is a possible route. Our results indicate that spherical, cylindrical, or lamellar nanostructures can be systematically formed based on blends with novolac and finally cross-linking the structures. Such nanostructures can basically be controlled similarly as the structures in the corresponding blends of thermoplastic polymers, knowing the molecular weight of P2VP block vs the novolac molecular weight before curing, molecular weight of the P2VP block vs the total molecular weight of P2VP-*block*-PI, and the weight fraction of PI in the final blend. The concept is fairly general and allows tailoring of the materials properties, as will be discussed in the forthcoming papers.

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