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Novel Amphiphilic Conetworks Composed of Telechelic Poly(ethylene oxide) and Three-Arm Star Polyisobutylene

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Amphiphilic polymers composed of hydrophilic and hydrophobic polymer chains, such as block copolymers, star blocks, core−shell structures, brushes, Janus micelles, and so forth, are of great interest from both fundamental scientific and many technological point of views for a large variety of applications ranging from surface-active materials to nanostructures (see, e.g., refs 1−7 and references therein). Amphiphilic conetworks (APCN),[8−31] that is, crosslinked polymers consisting of covalently bonded otherwise immiscible hydrophilic and hydrophobic chains, represent a new class of specialty materials able to interact with and to swell in both hydrophilic and hydrophobic media (for a recent review see ref 31). Recent structural investigations[19−21,23,32] by a variety of techniques (e.g., TEM, AFM, SAXS, SANS, and solid-state NMR) have revealed that the immiscible components form separate nanophases in such bicomponent conetworks. It has already been demonstrated that these new unique nanostructured materials can be used in a wide range of applications, such as controlled drug release matrixes,[8−10] biomaterials,[13,24] immunoisolatory devices,[14] contact lens materials,[15] pervaporation membranes,[17] and nanoreactors[19] for the preparation of novel organic−inorganic hybrids with nanocrystalline materials. Despite the unique properties and promising application possibilities, the synthetic process for obtaining APCNs is almost exclusively based on copolymerization of (meth)acrylate-telechelic macromonomers, for example, polyisobutylene,[8−14,18−20,32] poly(dimethylsiloxane),[15] polytetrahydrofuran,[16] polydioxolane,[21] polyoxazoline,[22] and poly(ethylene oxide),[23] with selected vinyl monomers yielding polymer chains with opposite philicity. This technique leads to conetworks in which the random crosslinking occurs by the telechelic macromonomer resulting in heterogeneous three-functional branching points. This method strongly limits the possibilities of the desired combinations of hydrophilic and hydrophobic polymers in APCNs since phase separation during syntheses and unsuitable reactivity ratios prevent the availability of a large number of APCN structures.

Coupling of hydrophilic and hydrophobic polymer chains with suitable functional groups may provide another, broadly applicable possibility for the synthesis of APCNs. However, there are only a few examples in the literature on the preparation of APCNs by coupling reactions of functional hydrophilic and hydrophobic chains with suitable terminal and/or pendant functionalities. Weber and Stadler[25] reported on the synthesis of polybutadiene-*l*-poly(ethylene oxide) (*l* stands for *linked*) APCNs by coupling polybutadiene with 1,2,4-triazoline-3,5-dione-telechelic poly(ethylene oxide) (PEO) via ene reaction. However, due to phase separation of the components even in a common solvent, they succeeded in incorporating only less than 20% PEO into such conetworks. In a similar way, Mikos and coworkers[26] obtained conetworks by crosslinking poly(propyl-

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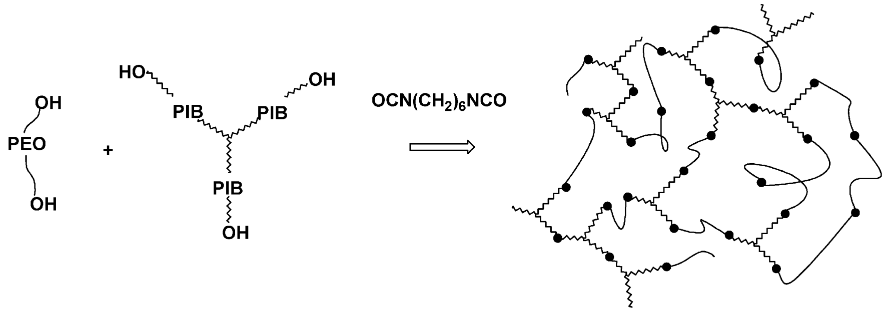
Scheme 1. Synthesis of PEO−PIB Amphiphilic Conetwork by Chain Coupling of Hydroxyl-Telechelic Poly(ethyleneoxide) (PEO) and Hydroxyl-Telechelic Three-Arm Star Polyisobutylene (PIB)[a]



[a] The dots indicate the coupling sites between the polymer chains.

ene fumarate) with methacrylate-telechelic PEO. Gitsov and Zhu[27] crosslinked telechelic PEO with hydrophobic amine-terminated dendritic (up to third generation) poly(benzyl ether)s. Hentze et al.[28] prepared ordered conetworks by γ-ray irradiation curing of poly(ethyleneoxide-*b*-butadiene) amphiphilic block copolymers. Recently, Patrickios and coworkers[29−31] have attempted to synthesize APCNs from endfunctional block copolymers consisting of poly(methyl methacrylate) and poly-[2-(*N*,*N*-dimethylamino)ethyl methacrylate] segments obtained by group transfer polymerization.

This study concerns a new approach for the synthesis of amphiphilic conetworks containing covalently bonded telechelic poly(ethylene oxide) (PEO) and three-arm star polyisobutylene (PIB) by using a chain coupling strategy yielding a structurally new generation of amphiphilic conetworks. PEO is a well-known strongly hydrophilic polymer while PIB is one of the most hydrophobic polymers. Thus, combination of these macromolecules in a conetwork is expected to result in unique new materials. Herein, we report on the successful synthesis and characterization of such PEO−PIB amphiphilic conetworks.

The well-known telechelic macromonomer method[8−23] applies radical copolymerization as a curing reaction of selected vinyl monomers with telechelic macromonomers. This random process yields conetworks with heterogeneous junction points. In general, homogeneous crosslinking points can be achieved by using three-arm, four-arm, and so forth or multi-arm star telechelic polymers or multifunctional coupling agents for coupling hydrophilic and hydrophobic polymers to form a conetwork. This synthetic strategy is shown in Scheme 1 for the preparation of PEO−PIB APCNs. In these conetworks the hydrophilic bifunctional linear PEO is coupled to hydrophobic three-arm star hydroxyl-telechelic PIB ($M_n = 1800$, $M_w/M_n = 1.08$, and functionality $F_n = 3.0$) obtained via quasiliving carbocationic polymerization of isobutylene and subsequent quantitative chain end derivatizations.[33,34] The coupling was achieved with stoichiometric amounts of diisocyanate in toluene as cosolvent for both polymers at 100 °C. The network forming homogeneous branching points are located at the center, that is, at the trifunctional initiating moiety of the PIB star polymer, and no other junction points are formed. The reaction of the isocyanate groups with primary alcohols is a selective and quantitative process resulting in perfect chain end coupling, and thus in a well-defined conetwork structure. As is depicted in Scheme 1, not only PEO−PIB coupling can occur but shorter and longer chain segments made of the same polymer type can also be formed. As a consequence, the length and composition between two crosslinking points can vary in wide ranges. This is the result of the random manner of the curing process which allows any of the hydroxyl-terminated chains to react with each other.

Table 1. Number Average Molecular Weights of the Starting PIB and PEO Samples, Amounts of Extractables, and PEO and PIB Contents of the PEO−PIB Amphiphilic Conetworks

samples	M_n (PIB)	M_n (PEO)	soluble part	PEO content	PIB content
R400	1800	400	42%	22%	61%
R1000	1800	1000	38%	36%	48%
R1450	1800	1450	39%	45%	40%

The composition of the PEO−PIB conetworks depends on either the molecular weight or the weight ratio of the reacting hydroxyl-telechelic PEO and PIB. However, if the relative amounts of these reactants were different from the stoichiometric 1:1 ratio with respect to the hydroxyl groups of PEO and the three-arm star PIB, then homocoupling of the polymer in excess was the dominating reaction. Although it is not possible to avoid completely these couplings, such reactions can be minimized when the concentrations of the PEO and PIB hydroxyl groups are the same. Therefore, syntheses of PEO−PIB APCNs were attempted between the three-arm star hydroxyl-telechelic PIB with $M_n = 1800$ and PEOs with different molecular weights (400, 1000, and 1450; the resulting conetworks are assigned with these numbers) with stoichiometric amounts of functional hydroxyl groups.

The molecular weights of the reacting polymers, the extractable amounts in THF, and the PEO and PIB contents of the final, extracted, and dried PEO−PIB conetworks are summarized in Table 1. After curing, the gels were first extracted with hexane and subsequently with water to remove unreacted PIB and PEO, respectively. These extractions gave only negligible amounts of extracts, indicating highly efficient coupling between PEO and PIB chains by the diisocyanate under the applied reaction conditions. However, when THF, a common solvent for both components, was used for

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extraction, fairly high, but nearly the same, amounts of extractable materials were obtained for the different samples, as shown in Table 1. As it is also listed in this table, the PEO and PIB contents are very close to the theoretical values in the PEO−PIB conetworks obtained after extraction with THF; that is, this process does not change the composition in the conetworks. On the basis of these findings, it can be concluded that the extractables in THF contain coupled PEO−PIB segments in the same ratio as in the corresponding conetworks. This was also confirmed by ^{1}H NMR analysis of the extracted materials, indicating that these polymers consist of PEO and PIB segments coupled by urethane linkages. It has to be noted that under certain conditions isocyanates can take part in side reactions resulting in allophanates or isocyanurates, which increase the crosslinking density if excess isocyanates are present.[35] On the other hand, protic impurities, such as water, or inadequate diisocyanate functionality can decrease the extent of crosslinking in such network-forming systems. Therefore, other than 1:1 isocyanate/hydroxyl group ratios were also tested for coupling PEO and PIB chains and evaluated by measuring the extractables from the resulting conetworks. It was found that minor changes in the stoichiometry did not have significant influence on the relative amounts of extractables, while higher than 10% excess of any of the reactants led to increased soluble fractions, that is, to decreasing the efficiency of network formation. The soluble fragments are either not fully extended polymers or macrocycles formed by cyclization between the terminal hydroxyl groups of branched PEO−PIB structures with low extent of coupling. The importance of cyclization on the extent of network formation from precursors with pre-existing branch points has been recently discussed by Dusek and Duskova-Smrckova.[36] It is important to note that the formation of macrocycles can be decreased by increasing the concentration of the reacting polymers. However, it was found by us that phase separation occurs at high polymer concentrations even in toluene, a good solvent for both polymers, due to the incompatibility of PEO and PIB. At low concentrations very high extractable parts can be measured or even gelation, that is, network formation, was not observed. Therefore, it is necessary to use as high polymer concentrations as possible for successful cocuring of hydroxyl-telechelic PEO and PIB. Orienting experiments showed us that phase separation does not take place at up to ~30% (w/v) overall concentration. As data indicate in Table 1, this optimal concentration yields PEO−PIB conetworks with expected compositions. In contrast to an earlier report[25] on polybutadiene-*l*-poly(ethylene oxide) conetworks with maximum 20% PEO content, in our case PEO−PIB conetworks were obtained with designed high PEO contents, that is, with 22−45% PEO in the examined materials.

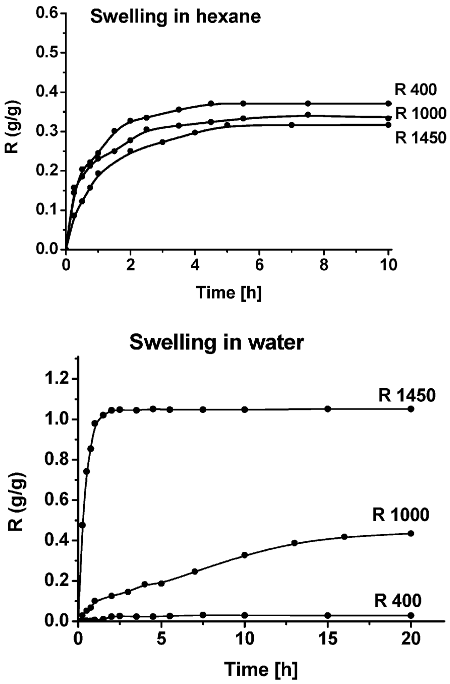

Figure 1. Swelling ratios of PEO−PIB amphiphilic conetworks in water and hexane as a function of time.

Table 2. Equilibrium Swelling Ratios of PEO−PIB Amphiphilic Conetworks

	hexane		water	
samples	R_{h}	$R_{\mathrm{PIB,h}}$	R_{w}	$R_{\mathrm{PEO,w}}$
R400	0.37	0.61	0.029	0.14
R1000	0.34	0.71	0.44	1.09
R1450	0.32	0.80	1.05	2.12

Swelling studies were carried out with the extracted and subsequently dried PEO−PIB conetworks in hydrophilic (water) and hydrophobic (hexane) solvents. The swelling ratios in water and in hexane as a function of time and the equilibrium swelling ratios are shown in Figure 1 and Table 2, respectively. As shown in Figure 1, all the PEO−PIB conetworks are swellable in both water and hexane. This proves the amphiphilic nature of these novel conetworks. The swelling data indicate several interesting aspects of the swelling behavior of the PEO−PIB amphiphilic conetworks. Swelling of the PIB phase in hexane occurs with relatively high rates, and the equilibrium swelling ratios are reached within a few hours. The equilibrium swelling ratio (R_{h} = weight of hexane/weight of conetwork) increases slightly with increasing PIB content. However, the normalized equilibrium swelling ratio ($R_{\mathrm{PIB,h}}$ = weight of hexane/weight of PIB in the conetwork) decreases with increasing PIB content, that is, with decreasing M_{c} (average molecular weight between crosslinks), as expected for conventional polymer networks.

In contrast to the swelling behavior in hexane, the swelling curves and equilibrium swelling ratios for the PEO−PIB APCNs in water strongly depend on the PEO content, that is, on the molecular weight of PEO in the conetworks as shown in Figure 1. Low swelling ratios were obtained in the case of the R400 sample. The R1000 conetwork swells with low rates before it reaches equilibrium. In contrast, the R1450 PEO−PIB conetwork rapidly swells in water, reaching more than 100% equilibrium swelling ratio. As data show in Table 2, both the equilibrium swelling ratios for the whole conetworks (R_{w} = weight of water/weight of network) and the equilibrium swelling ratios normalized to the PEO content ($R_{\mathrm{PEO,w}}$) increase with the PEO content, and

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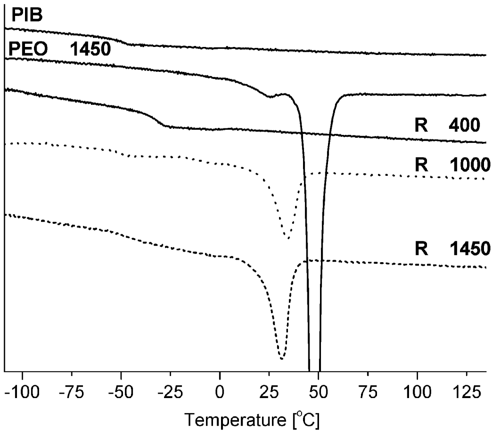

Figure 2. DSC curves of PEO−PIB amphiphilic conetworks and starting polymers (second heating, heating rate: 10 °C/min).

there are significant differences between the equilibrium swelling ratios in water for the different samples. In other words, the equilibrium swelling ratios can be controlled by the composition of the PEO−PIB APCNs.

There is an interesting feature of the swelling ratio versus time curves. For all the samples in the course of swelling in hexane, and for the R1000 sample in water somewhat strange swelling curves are obtained as shown in Figure 1. After an initial rapid swelling the swelling rate decreases for a period of time, and then it increases again before equilibrium swelling ratios are reached. This unusual swelling kinetics might be due to morphological and/or chain mobility changes in the PEO−PIB conetworks at a certain extent of swelling.

DSC analyses have also been carried out with the starting polymers and the dry PEO−PIB APCNs. The results of the DSC measurements for the starting PIB, PEO(1450), and the PEO−PIB conetworks are shown in Figure 2. DSC curves of APCNs reported so far show two distinct glass transition temperatures (T_g), indicating phase separation of the hydrophilic and hydrophobic polymer chains.[8,9,19,20,32] Glass transitions are observed in the case of every PEO−PIB conetworks at low temperatures in the range of the glass transition of the starting three-arm star hydroxyl-telechelic PIB ($T_g = -51$ °C) as shown in Figure 2. This indicates separate PIB domains in these conetworks. As has been reported,[25,37] the glass transition of low molecular weight PEOs in a conetwork is very broad and hardly observable. However, the existence of separate PEO domains is conclusively indicated by the melting peaks of PEO in the case of R1000 and R1450 conetworks. The pure PEOs with molecular weights of 1450 and 1000 have melting points (T_m) at 48 and 42 °C, respectively. The melting points of these polymers are shifted to lower values, that is, to 34 °C for PEO1450 and to 32 °C for PEO1000 in the corresponding PEO−PIB conetworks. This shift of T_m can most likely be attributed to the effect of the hydrophobic elastic PIB segments. It can also be seen in Figure 2 that the heights of the melting peaks of PEOs are significantly lower for the conetworks than that for the pure PEO. This means that the relative amounts of crystalline parts of PEO is suppressed by large extent as a consequence of connecting PEO1000 and PEO1450 in the PEO−PIB conetworks. The differences between the enthalpies of melting of the pure and network PEOs indicate that only ∼20% of PEO is crystalline in the conetworks. The R400 sample contains no detectable crystalline PEO, and the T_g of PIB is higher (−33 °C) than that of the starting PIB (−51 °C). This allows concluding that low molecular weight PEO chains are compatible at least in part with PIB in the conetwork.

In sum, a new approach, a chain coupling strategy, has been utilized by us to synthesize successfully a series of novel PEO−PIB amphiphilic conetworks (APCN) from exact telechelic polymers, i.e., from immiscible hydrophilic hydroxyl-telechelic PEO and strongly hydrophobic three-arm star hydroxyl-telechelic polyisobutylene with a diisocyanate coupling agent. This resulted in a structurally new generation of APCNs with homogeneous junction points located in the middle of the three-arm star PIB. It was found by us that although efficient coupling takes place, the extent of the gel fraction depends on the overall polymer concentration during crosslinking; the higher the concentration, the higher the gel fraction. However, there is a limiting concentration (∼30% in our case) since phase separation occurs above this concentration in common solvents, like toluene, for PEO and PIB due to the incompatibility of these polymers. Although the extractable part is relatively high compared to other synthesis strategies of amphiphilic conetworks by radical copolymerizations, it should be emphasized that the formed structures by coupling are superior to the previous conetwork types in its regularity, and the applied methodology can be easily adopted to a large variety of other types of hydrophilic−hydrophobic functional polymer pairs to build new amphiphilic conetwork structures. The resulting PEO−PIB conetworks reported in this study exhibit amphiphilic character, and the swelling behavior of these APCNs depends on composition. DSC measurements indicate phase separation between PEO and PIB, and significant suppression of crystallization of PEO in the PEO−PIB conetworks. These new materials are expected to be utilized in a wide variety of applications ranging from biomaterials to membranes, specialty polymeric templates, nanostructures, and so forth.

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Supporting Information Available: Additional experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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