Poly(methacrylic acid)-*l*-Polyisobutylene: A Novel Polyelectrolyte Amphiphilic Conetwork

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For the first time, a reliable procedure for synthesizing new acidic polyelectrolyte-containing amphiphilic conetworks (APCNs), poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB), is described. The thorough characterization of the synthesis products is also presented through elemental analysis, differential scanning calorimetry (DSC), and basic swelling studies. Three series of APCNs were successfully synthesized in wide composition ranges by the macromonomer method using exact bifunctional methacrylate-telechelic PIB cross-linkers (MA−PIB−MA) of three different molecular weights (M_n): 2000, 5000, and 13000. The MA−PIB−MA macromolecular cross-linkers were prepared via quasiliving carbocationic polymerization. To prevent phase separation and thus insufficient network formation during synthesis, the conetworks were synthesized by thermally initiated free radical copolymerization of MA−PIB−MA and trimethylsilyl methacrylate, a hydrophobized precursor of methacrylic acid. After the next critical synthetic step, the quantitative hydrolytic cleavage of the trimethylsilyl groups from the poly(trimethylsilyl methacrylate) chains in the resulting precursor conetworks, 5−8 different compositions of each PMAA-*l*-PIB conetwork series were obtained. The low amounts of extractables (<8−10%) and elemental analysis data showed high copolymerization yields and close to target compositions. DSC investigations indicated phase separation of the PMAA and PIB components. As all PMAA-*l*-PIB conetworks are optically clear materials, the extent of phase separation must occur on the nanometer scale. The amphiphilic character of these new materials was demonstrated by uniform swelling of PMAA-*l*-PIB conetworks in both aqueous and apolar media which indicates cocontinuous nanophasic morphology.

Introduction

Amphiphilic conetworks (APCNs) belong to a fairly new class of cross-linked polymers composed of covalently bonded hydrophilic and hydrophobic polymer chains.[1−35] Because they possess both hydrophilic and hydrophobic components, these materials are able to swell in and interact with both polar (aqueous) and apolar media. Inspired by an array of their diverse promising properties, such as nanophase-separated morphology,[12−17,33] controllable swelling behavior,[1−6] adaptable surface characteristics,[6] or advanced biocompatibility potential,[6,7,19,20] numerous application-oriented studies were focused on APCNs in recent years.

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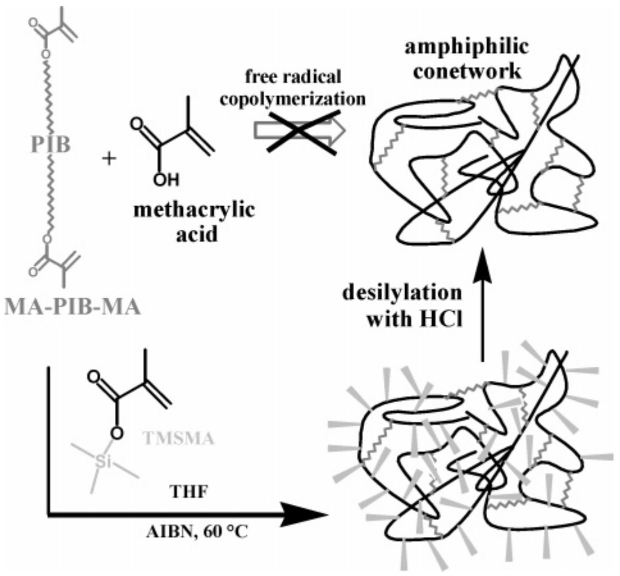
Some of these include the elaboration of nanoreactors for obtaining organic−inorganic hybrids with nanocrystalline materials,[12] medical implants and immunoisolation devices,[7,21] controlled drug delivery matrixes,[1,2] thermoresponsive gels,[22] cell culture surfaces,[19,20] contact lens materials,[8] pervaporation membranes,[10] solid-phase extraction,[23] highly oxygen-permeable membranes,[32] antifouling surfaces,[24] promoted release hosts,[25] and most recently the utilization of the large interphase area inside APCNs for increasing the efficiency of heterogeneous enzymatic catalysis.[26] The tendency of water-swollen APCNs to possess mechanical endurance superior to that of homopolymer hydrogels makes these materials particularly attractive candidates for a variety of applications. This enhanced mechanical strength is due to the reinforcing effect of the unsolvated hydrophobic component, which acts as a rubbery backbone and keeps the hydrophilic chains from overexpanding, thus preventing the gel from becoming excessively vulnerable to the type of disintegration that is common with most swollen hydrogels.

The greatest challenge of general APCN synthesis is the integration of the two chemically very different (hydrophilic and hydrophobic) polymer components. Since the composing chains in an APCN are thermodynamically incompatible, macroscopic phase separation is inevitable during the curing reaction (or already when trying to mix the components together) for many desired polymer combinations. This problem is especially acute when polymer chains of such different chemical nature are to be combined that they do not even have a commont solvent. Such is the case when trying to combine poly(methacrylic acid) (PMAA; a broadly applied component in many non-cross-linked polymers, especially in linear block copolymers; see ref 36 for a review) and polyisobutylene (PIB; one of the most hydrophobic polymers). Only one example[29] is known for PIB-based polyacid-containing APCNs (2-sulfoethyl methacrylate), but the composition control and reproducibility of these experiments has proved to be questionable.[37] In the present paper we report on the successful and reliable synthesis of a novel polymeric material, the poly(methacrylic acid)-*l*-polyisobutylene (PMAA-*l*-PIB) amphiphilic conetwork, which is composed of strongly hydrophilic PMAA (a polyelectrolyte) and extremely hydrophobic PIB ("*l*" stands for "*linked by*" [1]). The synthetic method presented is based on the modification of one component to make its polarity similar to that of the other component. That is, the hydrophilic monomer, and thus its resulting polymer chain, is hydrophobized to match its apolar counterpart. This procedure, which is also generally applicable to similarly incompatible combinations of polymers, is illustrated in Scheme 1. After synthesis in a broad composition range, thorough characterization of the resulting new materials was carried out, the results of which are also presented in detail.

Scheme 1. Synthesis of PMAA-*l*-PIB Amphiphilic Conetworks[a]



[a] Since direct reaction is not possible, the hydrophilic component is temporarily hydrophobized to prevent phase separation during component mixing and cross-linking.

Experimental Section

1. Materials. Methylmagnesium bromide (3.0 M solution in diethyl ether, Aldrich), 5-*tert*-butylisophthalic acid (98%, Aldrich), HCl (Messer), calcium chloride (anhydrous, Fluka), and ammonium chloride (puriss, Reanal) were used for the synthesis of the *tert*-butyldicumyl chloride initiator. Isobutylene (Messer), absolutized *n*-hexane (96%, Scharlau), absolutized dichloromethane (99.8%, Chemolab), titanium(IV) chloride (99.9%, Aldrich), redistilled *N*,*N*,*N*,*N*-tetramethylethylenediamine (99.5+%, Aldrich), allyltrimethylsilane (97+%, Fluka), aluminum oxide (activated, neutral, Brockmann I, STD grade, Aldrich), 9-borabicyclo[3.3.1]nonane (9-BBN; 0.5 M solution in THF, Aldrich), hydrogen peroxide (30 wt % solution in water, ACS reagent, Aldrich), freshly distilled methacryloyl chloride (99%, Aldrich), and distilled triethylamine (99%, Aldrich) were used to produce the MA−PIB−MA (MA = methacrylate) macromonomer. Trimethylsilyl methacrylate (TMSMA; 98%, Aldrich) was distilled under vacuum, tetrahydrofuran (THF; 99.8%, Chemolab) was refluxed over and distilled from potassium hydroxide (KOH; p.a., Merck), and α,α′-azobisisobutyronitrile (AIBN; 98+%, Fluka) was recrystallized twice from methanol (99.8%, Chemolab) for the curing reaction. A buffer solution (Aldrich) was used to set the pH constant at 7 for the swelling investigation.

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Table 1. Synthesis Feed Data for All Samples of the Three Series of PMAA-*l*-PIB APCNs (Columns 1−4)[a]

sample[b] (PIB 2K series)	MA−PIB−MA, 2K, mass (g)	TMSMA mass (g)	AIBN mass (mg)	conetwork composition,[c] % PIB
PMAA-*l*-PIB 11	0.20	1.42	1.55	11
PMAA-*l*-PIB 20	0.30	1.24	1.19	20
PMAA-*l*-PIB 35	0.40	1.06	0.88	35
PMAA-*l*-PIB 46	0.50	0.89	0.61	46
PMAA-*l*-PIB 58	0.60	0.71	0.39	58
PMAA-*l*-PIB 68	0.70	0.53	0.31	68
PMAA-*l*-PIB 78	0.80	0.35	0.16	78

sample (PIB 5K series)	MA−PIB−MA, 5K, mass (g)	TMSMA mass (g)	AIBN mass (mg)	conetwork composition,[c] % PIB
PMAA-*l*-PIB 27	0.30	1.25	1.19	27
PMAA-*l*-PIB 32	0.40	1.07	0.88	32
PMAA-*l*-PIB 47	0.50	0.87	0.61	47
PMAA-*l*-PIB 58	0.60	0.71	0.39	58
PMAA-*l*-PIB 67	0.70	0.54	0.31	67
PMAA-*l*-PIB 72	0.75	0.44	0.25	72
PMAA-*l*-PIB 76	0.80	0.36	0.16	76
PMAA-*l*-PIB 84	0.85	0.27	0.09	84

sample (PIB 13K series)	MA−PIB−MA, 13K, mass (g)	TMSMA mass (g)	AIBN mass (mg)	conetwork composition,[c] % PIB
PMAA-*l*-PIB 30	0.30	1.24	1.19	30
PMAA-*l*-PIB 39	0.40	1.06	0.88	39
PMAA-*l*-PIB 53	0.60	0.71	0.39	53
PMAA-*l*-PIB 63	0.70	0.53	0.31	63
PMAA-*l*-PIB 68	0.80	0.35	0.16	68

[a] Numbering in the conetwork name (column 1) refers to the final PIB content of the PMAA-*l*-PIB APCNs (%, m/m) as determined by elemental analysis (column 5). Column 2 displays the amount of PIB in the feed, which is also identical to the targeted PIB ratio in the conetworks. Column 3 shows the amount of TMSMA, calculated to complement the amount of PIB to obtain 1 g of each PMAA-*l*-PIB APCN after deprotection. The initiator quantity (column 4) is varied according to the composition ratios to ensure successful cross-linking. [b] Numbering refers to the PIB content in the PMAA-*l*-PIB conetworks (%, m/m). [c] Determined by elemental analysis.

2. Syntheses. Synthesis of the *tert*-butyldicumyl chloride initiator was carried out as reported previously.[38] The bifunctional methacrylate-telechelic PIB macromonomers (MA−PIB−MA) were obtained by quasiliving carbocationic polymerization[39] of isobutylene (initiated by the $TiCl_4$/*tert*-butyldicumyl chloride initiating system), a procedure especially apt for the synthesis of polymers with a narrow molecular weight distribution (MWD) and precise functionality. The polymerization reaction was followed by quantitative end group functionalization with allyltrimethylsilane.[38] The end groups of these allyl-telechelic PIBs were then modified by hydroboration, oxidation,[38−40] and methacrylation with methacryloyl chloride[41] to yield MA−PIB−MA of three different molecular weights (2070, 4900, and 13100, rounded to and denoted hereafter as 2K, 5K, and 13K). Polydispersity indices (M_w/M_n) of the same telechelic macromonomers were 1.04, 1.03, and 1.07, respectively (determined by gel permeation chromatography (GPC) analysis), while their functionality was uniformly 2.0 (confirmed by ^{1}H NMR).

For the conetwork synthesis, stock solutions were made from the MA−PIB−MA cross-linkers and the AIBN radical initiator in THF, while liquid TMSMA was used neat. These solutions and the liquid TMSMA were purged with nitrogen, and under an inert atmosphere, predetermined amounts were subsequently injected with a syringe into the holes of a Teflon mold, mixed, and sealed airtight. The quantity of TMSMA was calculated so that following deprotection the PMAA-*l*-PIB APCNs would each possess a targeted composition (see Table 1). The molds were kept at 60 °C for 72 h. After this curing reaction, the conetworks were removed from the mold, and THF was allowed to evaporate. The unreacted components were exhaustively extracted by soaking the conetworks in hexane three times for 24 h (hydrophobic extraction) and then by the ensuing deprotection step, which simultaneously also removed the hydrophilic residues. Deprotection (i.e., the removal of the $-Si(CH_3)_3$ groups) was accomplished by swelling the conetworks in a 5% solution of HCl in methanol, then in a solution of a 1:1 methanol/water mixture of the same HCl concentration, and finally in 5% HCl aqueous solution, twice for 24 h in each step. Following deprotection, the conetworks were washed by swelling them in a large excess of water five times for 24 h and then dried in vacuo until a constant weight was reached.

3. Characterization. Elemental analysis was performed with a Heraeus CHN-O-RAPID instrument by burning the samples in oxygen with a CuO catalyst.

Differential scanning calorimetry (DSC) analysis was carried out using a Mettler 4000TA thermal analyzer under a nitrogen atmosphere. The samples were heated from −120 to +170 °C with a heating rate of 10 °C/min, and the second run was recorded.

Swelling was studied by weighing vacuum-dried samples of roughly equal mass (∼50 mg) and similar geometries and then placing them in the solute. At set intervals each was taken out, blotted with tissue paper, and weighed before being reimmersed. Thus, the swelling degrees were determined gravimetrically as the percentage of solvent uptake compared to the mass of the dry conetwork and were recorded at controlled ambient temperature (21 °C) as a function of time until equilibrium was reached.

Results and Discussion

1. Synthesis Principles. The synthesis of PMAA-*l*-PIB APCNs was carried out via the so-called “macromonomer

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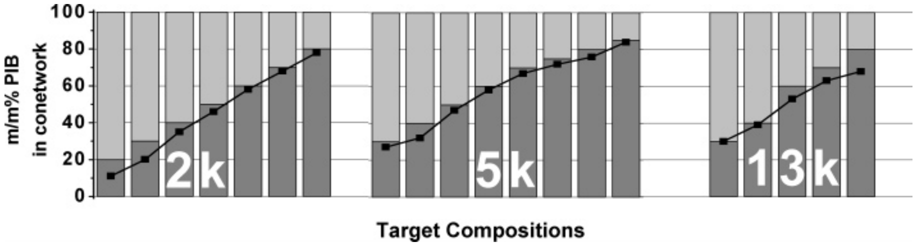

Figure 1. Comparison of target (bar graph) and actual (■) compositions for PMAA-*l*-PIB conetworks. Dark and light shadings of the bar graphs represent the planned respective ratios of PIB and PMAA in the conetworks. The reliability of the synthesis process is indicated by the actual conetwork compositions falling very near the target compositions.

method", which means copolymerizing a monomer with a bifunctional telechelic macromonomer, i.e., a polymer chain with a polymerizable functional group at each end. In the present case, this was MA−PIB−MA, a methacrylate-end-capped polyisobutylene (Scheme 1), which thus acts as a macromolecular cross-linker between two growing polymer chains. Provided that the proper synthetic parameters are met, this kind of copolymerization leads to the formation of polymer conetworks. The key issue in the synthesis of APCNs is to prevent phase separation of the two immiscible components before and during polymerization. One way of eliminating this fundamental problem is to temporarily modify one component to make its polarity and thus solubility similar to those of the other component. In the absence of a common solvent this method is also usually the only option. Scheme 1 shows that direct copolymerization of methacrylic acid (MAA) with MA−PIB−MA is not possible due to the lack of a common solvent for PIB and MAA (or PMAA). As is also exhibited in this scheme, to compatibilize the hydrophilic MAA with its hydrophobic counterpart, its acid functional group was modified to obtain a compound with a silyl protecting group,[42] providing an adequately hydrophobic monomer to be copolymerized with MA−PIB−MA. The silylated MAA (TMSMA) is sufficiently hydrophobic to avoid phase separation in a common solvent for all the components, that is, for MA−PIB−MA, TMSMA, and poly(trimethylsilyl methacrylate) (PTMSMA), during the copolymerization process. This way it was possible to form PIB-cured PTMSMA conetworks in a series of different compositions.

However, there are two other general requirements that must be met to ensure conetwork formation via the copolymerization reaction. The first requirement is that the telechelic macromonomer must possess precise functionality (in the present case 2.0). Otherwise it is prone to be inadequate to serve as a polymeric cross-linker; hence, conetwork formation will not take place. To obtain MA−PIB−MA with appropriate parameters, isobutylene was polymerized via quasiliving carbocationic polymerization,[39] a process especially suitable for the synthesis of telechelic macromonomers with well-defined functionality and chain length. This reaction yielded allyl-telechelic PIB,[38] which then underwent three quantitative end group modification reactions (hydroboration and oxidization followed by methacrylation) to obtain the desired MA−PIB−MA.[38−41] The completion of this reaction chain resulted in MA−PIB−MA telechelic macromonomers with a narrow molecular weight distribution (i.e., low polydispersity, $M_w/M_n < 1.10$) and precise functionality (2.0 per chain, ^{1}H NMR).

The other requirement for conetwork formation is that the growing polymer chains must be long enough to contain a sufficient number of cross-linking points to join with each other in a network. To ascertain this, kinetic control of the polymerization must be exercised, setting the chain length of PMAA to a value that ensures the incorporation of an adequate number of MA−PIB−MA macromonomer units. This chain length is determined by the average degree of polymerization (DP_n), so to achieve the appropriate PMAA chain length in each conetwork composition, it was this DP_n value that had to be controlled in each curing reaction. In free radical polymerizations, this is easily attained through varying the concentration of the initiator against that of the monomer (see $c_{\text{initiator}}$ in Table 1) on the basis of the formula $DP_n \approx c_{\text{monomer}}/(c_{\text{initiator}})^{1/2}$. Obviously, for the copolymerization to be successful, it is also imperative that both the macromonomer and the comonomer exhibit similar reactivity in the given polymerization reaction.

Last but not least, there is another critical factor for the successful synthesis of PMAA-*l*-PIB-type conetworks: efficient removal and transformation of the hydophobic protecting groups, in our case the trimethylsilyl groups, as shown in Scheme 1. Due to the easy hydrolytic cleavage of the C−O−Si bond,[42] this was achieved by sequential acidic hydrolysis. First methanol, then a 1:1 methanol/water mixture, and finally water were used as the solvent. This series of steps was necessary because methanol is better suited for the fast and thorough penetration into the PTMSMA-containing conetworks. Then, as the gels become increasingly hydrophilic with the ongoing removal of the $-Si(CH_3)_3$ groups, water gradually becomes a superior swelling agent, facilitating the complete removal of the protecting groups in the swollen conetworks.

2. PMAA-*l*-PIB Conetwork Compositions. The resulting dry conetworks were macroscopically homogeneous, tough, transparent solid disks, which subsequently underwent elemental analysis. From the elemental analyses, the actual PIB content of the PMAA-*l*-PIB APCNs was determined (%, m/m, also displayed in the sample names). These results are shown in Table 1 and Figure 1, both of which also show a comparison of the final conetwork compositions with the target compositions. It can be seen that, independent of the molecular weight of the MA−PIB−MA cross-linker used,

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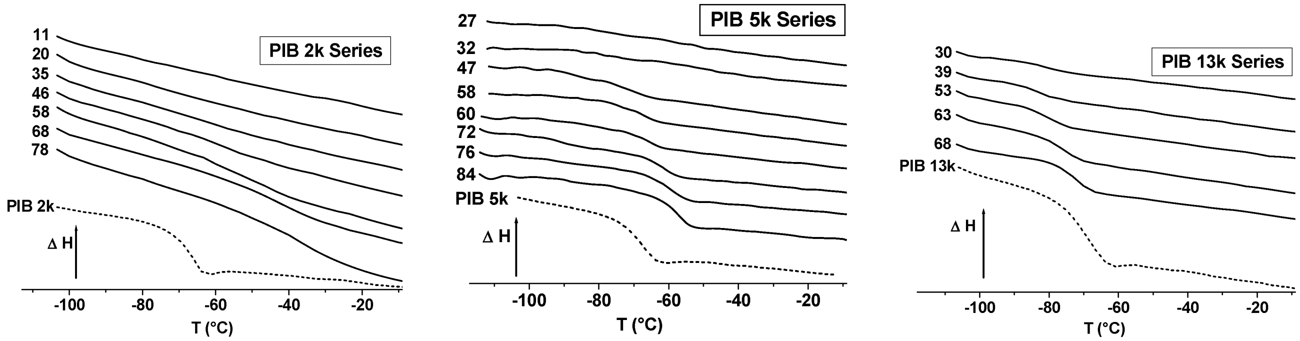

Figure 2. DSC traces of PMAA-*l*-PIB conetwork samples of different compositions from all three series (PIB 2K, 5K, and 13K) of conetworks (heating rate 10 °C/min). The clear T_g signals in samples with medium to high PIB content indicate the presence of a pure PIB phase, which suggests phase-separated morphology. At low PIB contents, PIB glass transitions are faint and elongated.

the actual conetwork composition ratios evidently follow the planned values closely and consistently. Coupled with low extractables data (typically under 8−10%), these results indicate near-quantitative copolymerization yields and also quantitative deprotection. The incorporation of PIB is always somewhat lower than planned. This is thought to be primarily attributed to the slightly lower reactivity of the considerably larger MA−PIB−MA macromonomer compared to that of the TMSMA comonomer (see ref 33 for the role of the macromonomer molecular weight on its reactivity in conetwork formation). On the basis of the close correspondence between the data of synthesis and elemental analysis, it can be concluded that the synthetic procedure devised is a very reliable and well-reproducible method for the production of PMAA-*l*-PIB APCNs in broad composition ranges and with different molecular weight PIB macromolecular cross-linkers.

3. Characterization. *3.1. Differential Scanning Calorimetry*. The DSC traces of the PMAA-*l*-PIB samples prepared are shown in Figure 2. Because of the thermodynamic incompatibility between the two components, their phases are expected to segregate as much as their chain segment mobilities (restrained by the cross-linking) will allow them. Certainly, a glass transition temperature (T_g) in the same region as that of pure PIB (∼−68 °C) is visible on the DSC traces, the intensity of the signal being proportional to the amount of PIB in the conetworks. The T_g belonging to the other component, PMAA (around 228 °C, extrapolated data[43]), is not detectable by DSC because it is above the decomposition temperature of this polymer. At low PIB content the T_g signal is, though detectable, faint and elongated. In these cases, due to the small amount of target sample present, the intensity of the PIB T_g signal is near the detection limits of the DSC instrument. Nonetheless, at higher magnification of these traces or by software analysis the glass transitions of PIB are still clearly discernible. Samples containing medium to high PIB contents however exhibit a very clear glass transition. The presence of glass transition signals for PIB in the conetworks indicates that the two components (PIB and PMAA) are phase separated. Considering that the samples are macroscopically homogeneous and optically clear (transparent), the DSC results suggest that this phase separation takes place on a scale below the wavelength of visible light, that is, macroscopic phase separation is absent, and separate PMAA and PIB phases exist on the nanometer scale in the PMAA-*l*-PIB conetworks.

3.2. Swelling of PMAA-l-PIB Conetworks. The amphiphilic character of APCNs is demonstrated by their ability to swell in both aqueous and apolar media, as presented in Figure 3. The graphs shown here portray the equilibrium swelling degrees of all three series of PMAA-*l*-PIB conetworks as a function of composition (%, m/m, PIB content) in water (at pH 7, Figure 3a) and in *n*-hexane (Figure 3b). Swelling of the APCNs in each solvent occurs via the solvation of the chemically appropriate polymer chain. The normalized swelling data are also shown (hollow squares). These represent the swelling degree values for gels of each composition normalized to the corresponding solvated polymer content (i.e., to 100%, m/m, PMAA content in aqueous media and to 100%, m/m, PIB in *n*-hexane). Normalization of the swelling data is useful because this way the trivial effect of the composition on the swelling degree can be easily eliminated. In other words, in the hypothetical case where no additional structural changes would entail the variation of component ratios, the doubling of the PMAA ratio in an APCN, for example, would result in the doubling of the actual aqueous swelling degree, while the normalized swelling data would remain unchanged. One such case can be observed in the aqueous swelling behavior of the PIB 5K series in the 65−85%, m/m, PIB composition range (Figure 3a). The normalized swelling degree stays constant, indicating that no fundamental structural differences are present in the swollen conetworks of this composition region. However, apart from this particular case, it can be concluded that since not only the actual but also the normalized swelling degrees change considerably with composition, significant structural differences exist between the swollen conetworks of each composition. These structural differences most likely comprise variations in the cross-link density, chain segment mobilities, and phase integrities of the two components within the conetworks. The complex effect of these factors can also be seen in the hydrophobic swelling behavior of PMAA-*l*-PIB conetworks. If, like in homopolymer networks, swelling depended only on the cross-link density, or the structural parameter which is most closely related to it, i.e., the molecular weight of the appropriate chain segments between cross-linking points, then the normalized apolar

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(43) Razinskaya, I. N.; Kharintonova, N. E.; Shtarkman, B. P. *Vysokomol. Soedin.* **1969**, *B11*, 892.

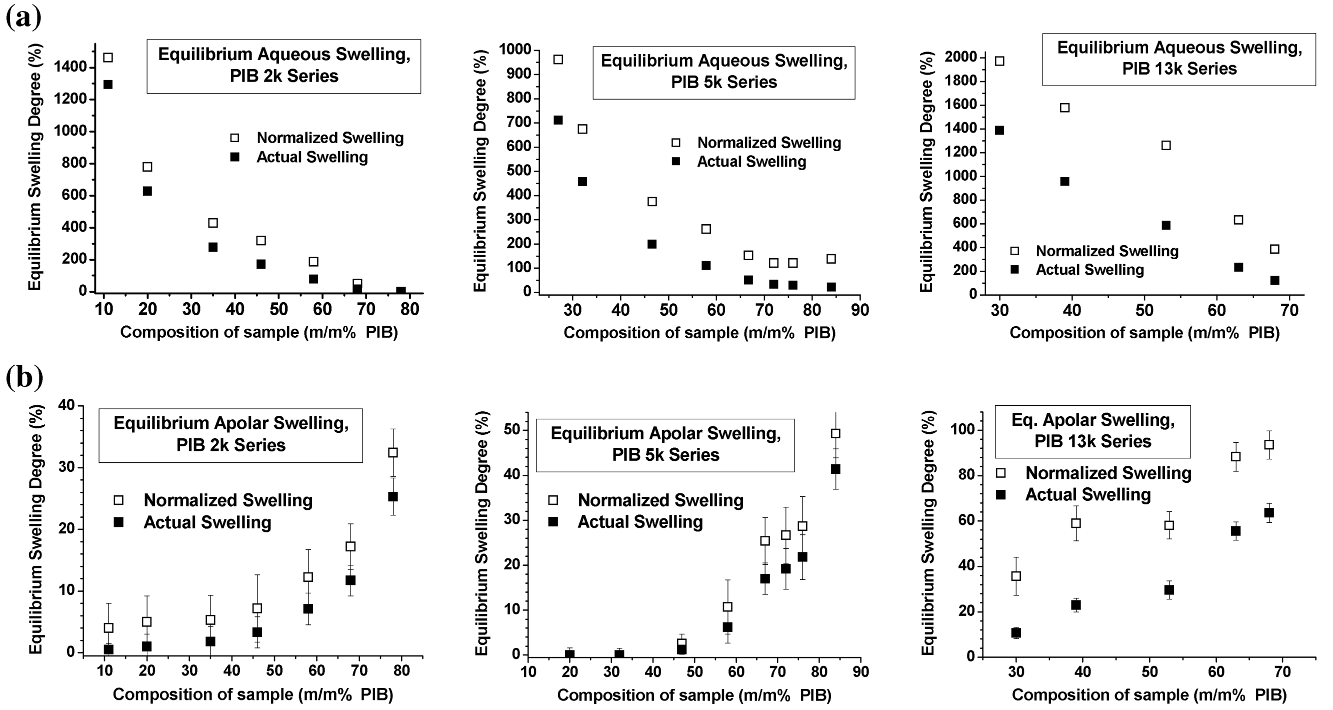

Figure 3. Normalized (□) and actual (■) equilibrium swelling degrees of PMAA-*l*-PIB amphiphilic conetworks of all three series (PIB 2K, 5K, and 13K) as a function of PIB content: (a) in aqueous media (at pH 7), (b) in apolar media (*n*-hexane).

equilibrium swelling degree would be constant in each conetwork series, as the molecular weight of the PIB segments is constant (2K, 5K, or 13K). However, it is apparent in Figure 3b that the normalized apolar equilibrium swelling degree changes with composition, indicating that hydrophobic swelling is a composite function of various structural parameters as listed above.

Aside from the recognition of amphiphilic swelling behavior, the following additional observations can be made concerning the diagrams displayed in Figure 3. First, it can be concluded that equilibrium swelling is always a function of composition. In each solvent it increases with an increase of the ratio of the solvated conetwork component. This relation is important because it offers a definite means of control over the swelling properties via composition parameters. Further, the generally nonlinear change of equilibrium and normalized swelling degrees with regard to composition suggests that the swelling behavior is influenced in a complex way by several composition-related factors, such as the overall conetwork philicity, cross-link density, and phase morphology. To assist in interpreting the particular shapes of the swelling curves, basic phase morphological considerations offer some explanations. For example, swelling in organic solvent (Figure 3b) is limited by the expansion capacity of the PIB phase within the conetwork, which in turn is determined by the coherence of the glassy PMAA phase. When the PMAA phase is coherent, its glassy structure uncompromisingly confines the solvated PIB, and the conetwork is so rigid that no distortion in its structure can occur. Thus, the absence or a low extent of hydrophobic swelling can be detected when PMAA makes up the significant majority of the conetwork. However, with an increase of PIB in the composition ratio, the integrity of the PMAA phase diminishes, and apolar swelling becomes possible. In the case of the PIB 13K series, significant apolar swelling already occurs at lower PIB contents. This is likely due to the low degree of cross-linking and the resulting high chain segment mobility that is characteristic of the structures comprising this conetwork series. These properties provide adequate expansion capacity for the PIB phase even at a high PMAA content. The connection between apolar swelling capability and PIB phase mobility is also suggested by comparing the diagrams in Figure 3b with the DSC curves in Figure 2. The PMAA-*l*-PIB samples displaying a clear PIB T_g also tend to show significant apolar swelling and vice versa. Further, the effect of segment and phase mobilities on both apolar and aqueous swelling degrees is reflected in the general dependence of equilibrium swelling ratios on the length of the PIB cross-linker. The use of a high molecular weight PIB cross-linker results in a looser conetwork structure; therefore, at identical (interpolated) weight ratio compositions of the conetworks, the samples containing longer PIB segments always exhibit higher degrees of swelling. The uniform swelling of PMAA-*l*-PIB conetworks in both hydrophilic and hydrophobic solvents in a wide composition range indicates the existence of cocontinuous (bicontinuous) nanophases in these new materials. More in-depth investigation into the morphology and swelling behavior of these APCNs (including pH dependence) will comprise the focus of further research.

Conclusions

Novel PMAA-*l*-PIB polyelectrolyte-containing amphiphilic conetworks with well-defined structures (in terms of the cross-link density and length of the comprising polymer chains) were successfully synthesized in broad composition ranges, resulting in a multitude of unique independent polymer structures. Synthesis involved the copolymerization of exact telechelic MA–PIB–MA macromolecular cross-linkers with a protected (silylated) comonomer, trimethylsilyl methacrylate, followed by quantitative deprotection in the resulting precursor conetworks. The synthetic method proved to be very reliable and fully reproducible; elemental analysis indicated almost on-target synthesis. DSC scans of these new PMAA-*l*-PIB conetworks showed phase-separated morphology, and this finding was amended by swelling experiments, which allowed the conclusion that not only are the component phases separated, but each of them is continuous over a wide composition range. The amphiphilic character of the PMAA-*l*-PIB conetworks was demonstrated by swelling them in both water and *n*-hexane. Since the synthetic method described is broadly applicable, it opens many exciting possibilities for producing further unique materials. The wide variety of PMAA-*l*-PIB APCN compositions with various PIB cross-linker lengths opens a wide potential for thorough correlation analysis of material properties with structural parameters in future studies of this promisingly versatile, novel polymer conetwork.

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