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Amphiphilic networks. XIV

Synthesis and characterization of poly(*N,N*-dimethylacryl-amide)-*l*-three-arm star polyisobutylene

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Summary
The synthesis and characterization of novel amphiphilic networks based on dimethylacrylamide and crosslinked by methacrylate telechelic three-arm star polyisobutylene ($\varnothing$(PIB-MA)$_3$) are reported. The networks are characterized by two M_c's and possess "homogeneous" and "heterogeneous" crosslinks. The networks swell both in water and *n*-heptane which indicates a cocontinuous hydrophobic-hydrophilic microarchitecture. Water-swollen networks exhibit higher tensile strengths and elongations, than those made previously with linear MA-PIB-MA's of similar overall compositions (i.e., ~1.0 versus ~0.5 Mpa, and ~300% versus ~200%, respectively). The enhanced mechanical properties of the new networks are being exploited in biomedical applications.

Introduction
Amphiphilic networks comprising hydrophilic polyacrylate main chains crosslinked by MA-PIB-MA's are biocompatible and avascular, and were found to be suitable for the preparation of immunoisolation of pancreatic islets [1-3]. The tensile strengths of highly water-swollen immunoisolatory membranes, however, are rather low, ~0.5 MPa [4]. We theorized that the mechanical properties of our membranes could be improved with more efficient crosslinking, specifically by substituting the two-functional MA-PIB-MA with three-functional crosslinking agents $\varnothing$(PIB-MA)$_3$, Thus the objectives of the present study were to synthesize and characterize amphiphilic networks of dimethylacrylamide (DMAAm) crosslinked by $\varnothing$(PIB-MA)$_3$'s, to study their swelling behavior in water and in *n*-heptane, and to investigate their mechanical properties in the dry and wet state.

Experimental
1. Materials
Tricumyl chloride (TCC) was synthesized by the procedure of Mishra et al. [5]. DMAAm (Aldrich, 99%) was distilled under vacuum before use (bp.= 80-81 °C at 20 Hgmm). Benzoyl peroxide (BPO) (Aldrich, 97%), N,N-dimethyl-p-toluidine (DMT) (Aldrich,

[*] For paper XIII in this series see J.P. Kennedy, G. Fenyvesi, S. Na, B. Keszler, and K.S. Rosenthal, Designed Monomers and Polymers, in press

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99%), methanol (Aldrich, 99%), hexanes (Aldrich, 95%), and heptane (Aldrich, 99+%) were used as received. Tetrahydrofuran (THF) (Aldrich, (99.9+%) was distilled over calcium hydride before use.

2. Network Synthesis

The synthesis of the three-arm star allyl-telechelic PIB ($\varnothing$(PIB-MA)$_3$) was carried out by living cationic polymerization using the TCC/$TiCl_4$/N,N-dimethylacetamide/ -80°C system [6-8] and end-quenching with allyltrimethylsilane [9]. The functionalization of the allyl-tri-telechelic PIB to ($\varnothing$(PIB-MA)$_3$) has been described [10].

The PDMAAm - *l* - three-arm star PIB networks were prepared by BPO induced free radical copolymerization of DMAAm with $\varnothing$(PIB-MA)$_3$ of M_n= 4500, M_w/M_n= 1.12; M_n= 10200, M_w/M_n= 1.07; M_n= 15000, M_w/M_n = 1.04, in THF at 40 °C for 24 hrs. Initiation was accelerated by DMT. Polymers were extracted sequentially with hexane and methanol for 24 hrs to remove unreacted $\varnothing$(PIB-MA)$_3$, DMAAm and PDMAAm, respectively. The first three columns of Table 1 identify the networks by the usual code [1], and specifies the composition of the charges.

Networks for swelling experiment were synthesized in vials (2 dram size), while those for tensile-strength measurements were prepared in rectangular, 9x14 cm Teflon molds sealed with Teflon coated Al-foil.

3. Characterization

Dried and preweighed disc shaped samples of polymer networks (11mm diam., 3mm thick) were placed in *n*-heptane and distilled water, respectively, at room temperature (~22°C). Samples were periodically removed from the swelling media, the excess liquid was removed by blotting with tissue paper, and weighed. Swelling kinetics were obtained by plotting the swelling ratio Q(t), i.e.(g solvent adsorbed at time t)/(g dry network), versus time.

Tensile properties were obtained by an Instron 5567 Tensometer with a 5kg-load cell and at a crosshead speed of 50mm/min, with 30mm clamp separation. Strain was measured by a Video Extensometer at a calculated strain rate of 1.67min^{-1}. A minimum of three microdumbells (ASTM D638-5) of networks containing 50% PIB were tested and their averages are reported. Stresses and elongations were recorded for each sample.

Results and Discussion

1. Synthesis and Molecular Characterization

A series of amphiphilic networks with varying compositions were synthesized by the copolymerization/crosslinking of DMAAm with various molecular weight $\varnothing$(PIB-MA)$_3$. The first column in Table 1 contains the networks code, (A stands for the monomer DMAAm, the first digit x 1000 gives the M_n of the PIB, and the second digit shows the PIB wt% in the network) and the second and third columns give feed compositions. In the fourth to seventh columns we summarize the amounts of hexanes and methanol soluble fractions, and the compositions of the networks after extraction. The last two columns give the theoretical M_c's of hydrophilic chain segments and crosslink density, respectively, assuming complete $\varnothing$(PIB-MA)$_3$ incorporation.

The amount of hexanes soluble fractions increased with increasing PIB content and molecular weight. The increasing amounts of PIB may decrease the accessibility of the

reactive MA groups of the crosslinking agent during synthesis. The amounts of methanol soluble fractions follow the opposite trend.

Networks containing the ∅(PIB-MA)$_3$ crosslinking agent possess two kinds of crosslinks i.e., a "homogeneous" and a "heterogenous" crosslink, and are characterized by two M_c's. Figure 1 helps to visualize the scheme of such a network. The core of the ∅(PIB-MA)$_3$ (i.e., the initiator fragment that remains in the three-arm star PIB) is a homogenous

Table 1. Characteristics of amphiphilic networks

Network	Feed composition Ø(PIB-MA)$_3$ g	DMAAm g	Hexane extract %	Methanol extract %	Network composition[b] PIB(MA)$_3$ %	DMAAm %	$M_{c,PDMAAm}$[b] g/mol	Crosslink Density[c] mol/g x 10^4
A-4.5-30	0.0600	0.1400	2.41	4.31	30	70	3500	2.67
A-4.5-40	0.0800	0.1200	3.82	3.80	40	60	2250	3.56
A-4.5-50	0.1000	0.1000	4.25	2.59	50	50	1500	4.44
A-4.5-60	0.1200	0.0800	4.60	1.28	59	41	1040	5.24
A-10-30	0.0600	0.1400	2.52	5.48	31	69	7420	1.24
A-10-40	0.0800	0.1200	4.37	5.27	40	60	5000	1.60
A-10-50	0.1000	0.1000	5.10	4.63	50	50	3330	2.00
A-10-60	0.1200	0.0800	5.70	2.19	59	41	2320	2.36
A-15-30	0.0600	0.1400	3.65	7.88	31	69	11130	0.83
A-15-40	0.0800	0.1200	5.18	7.15	41	59	7200	1.09
A-15-50	0.1000	0.1000	6.35	5.59	50	50	5000	1.33
A-15-60	0.1200	0.0800	7.43	4.20	59	41	3470	1.57

[a]Copolymerization initiated by 0.0045g BPO in the presence of 0.0075g DMT in 0.7mL THF, at 40°C for 24 hrs,
[b]Corrected by extraction results,
[c]Calculated, see text for assumptions.

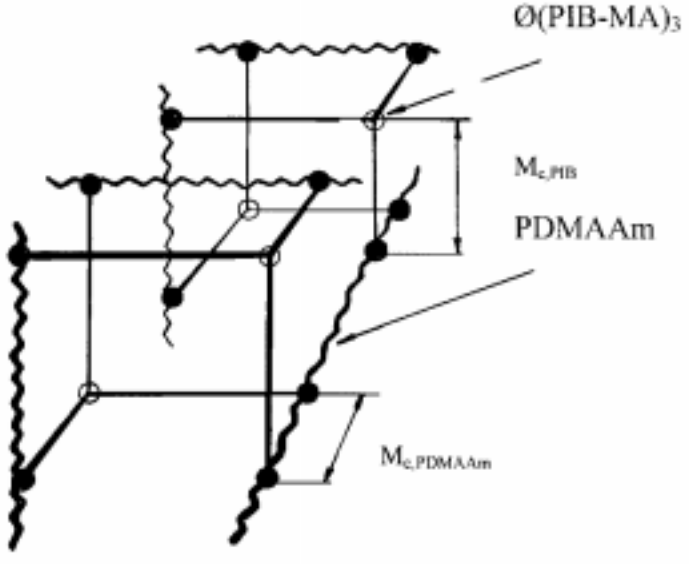
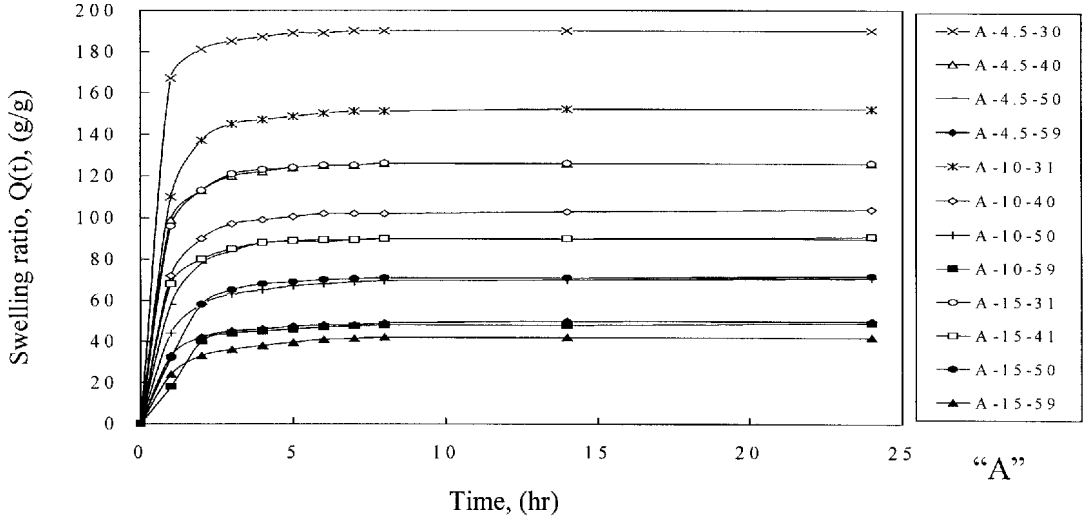


Figure 1. Scheme of amphiphilic networks based on Ø(PIB-MA)$_3$. Strait lines = PIB, wiggly lines = PDMAAm; • = homogeneous crosslink points, O = heterogeneous crosslink points.

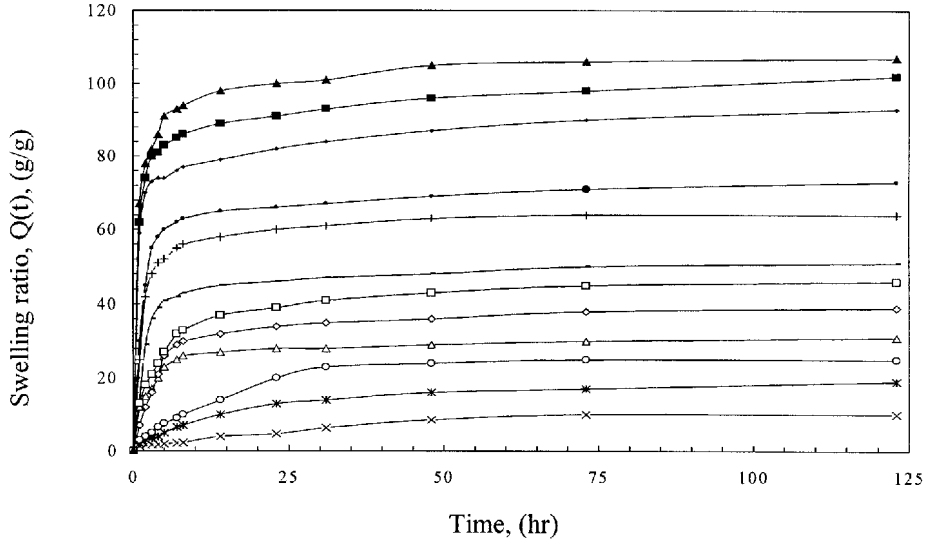
crosslink point connecting only hydrophobic segments. In contrast, the incorporation of the ∅(PIB-MA)$_3$ into the growing PDMAAm chains creates heterogeneous crosslink.
points that connect hydrophilic and hydrophobic segments. $M_{c,PIB}$ is the molecular weight of one arm of the three-arm star PIB, while $M_{c,PDMAAm}$ is the molecular weight of the PDMAAm segment between two heterogeneous crosslinks. Assuming complete ∅(PIB-MA)$_3$ incorporation, the $M_{c,PDMAAm}$ and the crosslink density of the networks can be calculated from the overall composition and the molecular weight of the PIB:

$$M_{c,PDMAAm} = \frac{M_{n,DMAAm}}{3X} = \frac{M_{n,PIB}PDMAAm\%}{3PIB\%}$$

where $M_{n,DMAAm}$ is the molecular weight of the DMAAm monomer, X is the crosslink concentration (mol crosslinker / mol monomer), and 3 stands for the functionality of the a



"A"



"B"

Figure 2A and 2B. Swelling of A-networks in water and *n*-heptane

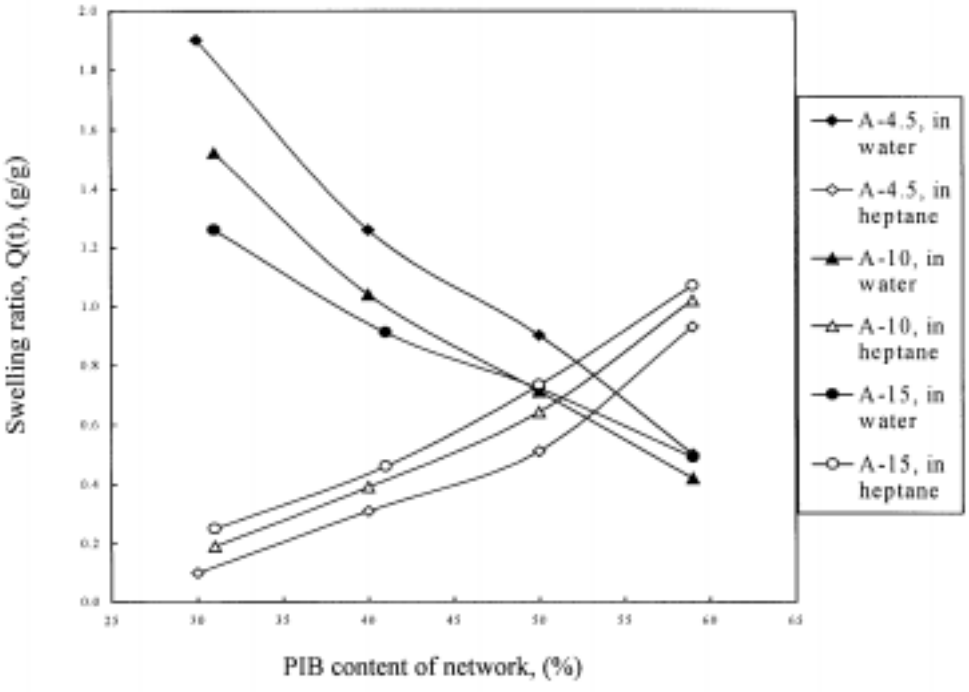


Figure 4. Equilibrium Swelling of A- networks in water and *n*-heptane

∅(PIB-MA)$_3$, $M_{n,PIB}$ is molecular weight of the PIB and PDMAAm% and PIB% are the wt% PDMAAm and PIB in the network, respectively. The theoretical crosslink density of perfect network is equal to the number of crosslinks per unit weight of the network. Table 1 shows these calculated values. While $M_{c,PDMAAm}$ decreases with increasing PIB content and increases with increasing PIB molecular weight, the crosslink density increases with increasing PIB content and decreases with increasing PIB molecular weight. Networks based on ∅(PIB-MA)$_3$ have lower $M_{c,PDMAAm}$'s and higher crosslink densities than networks based on linear MA-PIB-MA [4].

2. Swelling Studies

Figures 2A and 2B show swelling profiles of amphiphilic networks in water and *n*-heptane, respectively. Swelling in water reaches equilibria in ~14 hours, while in *n*-heptane it requires in most cases more than ~72 hours. As expected, swelling increases in *n*-heptane and decreases in water with increasing PIB content. Figure 3 is a summary of the equilibrium swelling data obtained from the swelling curves shown in Figures 2A and 2B. Equilibrium swelling in *n*-heptane increases with increasing molecular weight of ∅(PIB-MA)$_3$, and reaches a higher value than in networks of the same compositions obtained with linear PIB [11]. The equilibrium swelling in water follows the opposite trend, that is swelling increases with decreasing PIB molecular weight. Networks crosslinked by three-arm star PIB's swell less or equal in water than networks made with linear PIB of the same M_n [11].

3. Mechanical Properties

Figure 4 shows stress-strain traces of a series of dry and networks crosslinked with different molecular weight ∅(PIB-MA)$_3$ (i.e., M_n = 4,500, 10,200, and 15,000 g/mol) but

having essentially the same overall compositions (i.e., hydrophile/hydrophobe content 50/50). Table 2 lists ultimate stresses and elongations together with similar data obtained with networks crosslinked with linear MA-PIB-MA of M_n = 4,500, and 10,000 g/mol with 50/50 and 43/57 hydrophile/hydrophobe compositions.

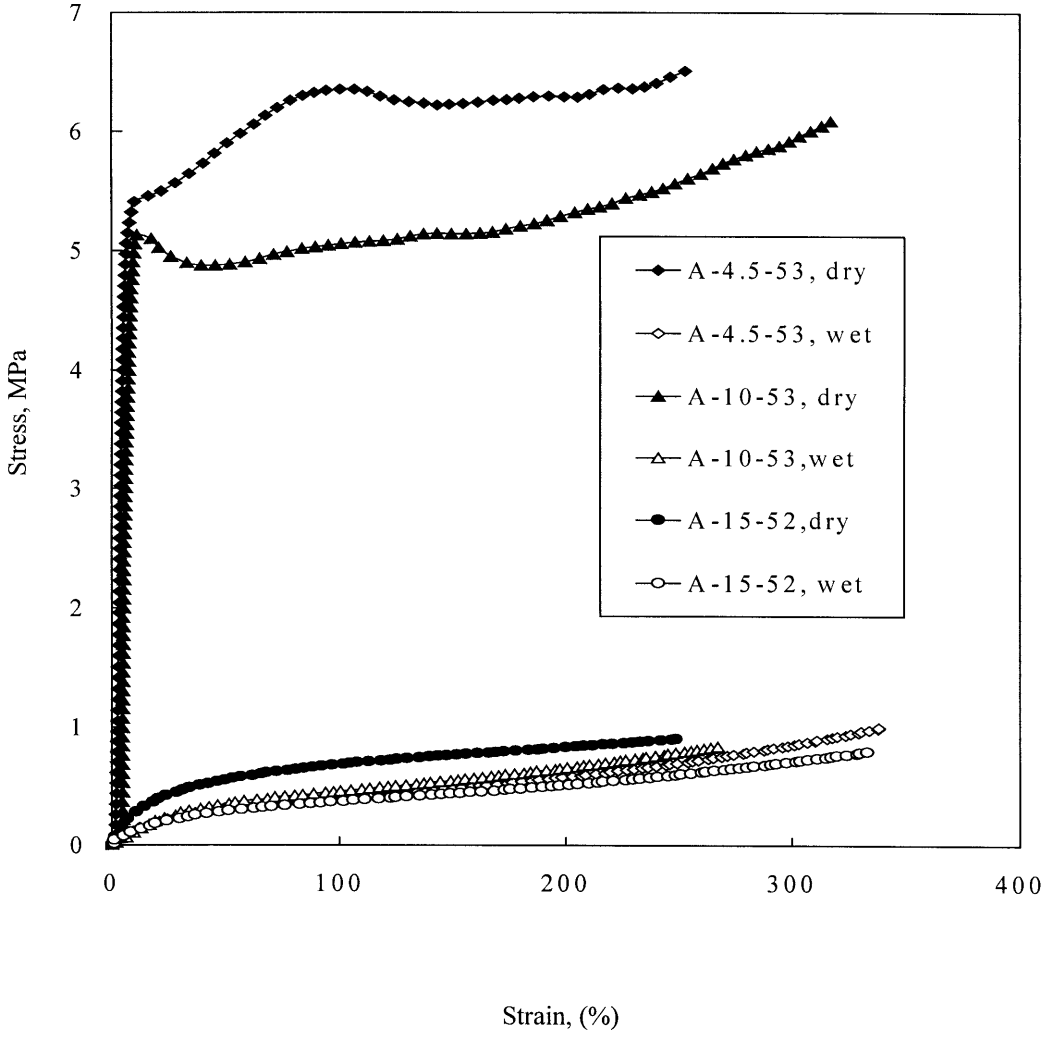


Figure 4. Stress-strain curves of a series of dry and wet networks

The stress-strain curves of networks obtained with ∅(PIB-MA)$_3$ of M_n = 4,500 and 10,000 g/mol exhibit yield points followed by complex rubbery behavior. As expected, for dry samples the tensile strengths decrease and elongations increase with increasing M_n of the PIB crosslinking agent, due to the decreasing crosslink densities. However, these values are considerably lower, than those of the corresponding networks prepared with linear PIB [4].

Water-swollen networks obtained with ∅(PIB-MA)$_3$ exhibit higher tensile strengths and higher elongations of the same $M_{n,PIB}$ than those made with linear MA-PIB-MA.

Evidently, the swelling behavior of these networks are different. Due to their lower or

Table 2. Mechanical properties of A-networks

Network	Type of PIB in network	Stress at break, Mpa		Strain at break,%	
		dry	wet	dry	wet
A-4.5-52	Ø(PIB-MA)$_3$	6.51	1.00	253	250
A-10-53	Ø(PIB-MA)$_3$	6.03	0.84	314	268
A-15-52	Ø(PIB-MA)$_3$	0.98	0.83	320	297
A-4.5-50	MA-PIB-MA	16.67	0.46	113	116
A-10-57	MA-PIB-MA	17.16	0.58	198	205

equal swelling in water but higher crosslink densities, these networks with the three-functional crosslinker retain more of their original strength than those obtained with linear PIB.

Conclusion

New amphiphilic networks based on three-arm star PIB were synthesized. We theorized that by applying methacrylate telechelic three-arm star PIB crosslinker, PIB incorporation into the network will improve and give rise to better mechanical properties, especially when these networks are swollen in water. We have found that because of the shorter $M_{c,PDMAAm}$ and higher crosslink densities, the tensile strength of networks crosslinked by the 3-functional ∅(PIB-MA)$_3$ were lower than the corresponding ones prepared with linear MA-PIB-MA. Morover, for the same reasons, and because the novel networks swell less or equal in water, they also exhibit higher strength in the water-swollen state. This important characteristics of the networks will be exploited in future biomedical applications.

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