Polymer Bulletin 48, 475–482 (2002)

Polymer Bulletin

Novel amphiphilic membranes of poly(N,N-dimethyl acrylamide) crosslinked with octa-methacrylate-telechelic polyisobutylene stars*

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Received: 30 January 2002 / Revised version: 6 May 2002 / Accepted: 7 May 2002

Summary

A series of novel amphiphilic networks were synthesized by free-radical mediated copolymerization/crosslinking of N,N-dimethyl acrylamide (DMAAm) with various molecular weight octa-methacrylate telechelic polyisobutylene stars ($PIB(MA)_8$) as crosslinking agents. The overall composition of the PDMAAm-*l*-$PIB(MA)_8$ networks were controlled by controlling the concentration of the starting materials. Crosslinking was essentially complete as indicated by negligible sol fractions in both methanol and *n*-hexane. Swelling ratios and swelling rates of various PDMAAm-*l*-$PIB(MA)_8$ in water and *n*-heptane were determined and contrasted with those of networks prepared with di- and tri-methacrylate-telechelic PIB croslinkers ($PIB(MA)_2$ and $PIB(MA)_3$). The mechanical properties of water-swollen tubules made of PDMAAm-*l*-$PIB(MA)_8$ were studied and compared with tubules made with $PIB(MA)_2$ and $PIB(MA)_3$.

Introduction

In the course of our continuing investigations of amphiphilic membranes for biological applications [1-3], we have recently prepared membranes consisting of poly(N,N-dimethyl acrylamide) (DMAAm) main chains crosslinked by octa-methacrylate-telechelic polyisobutylene stars ($PIB(MA)_8$). The impetus for this research was our belief that networks crosslinked by octa-telechelic stars will exhibit superior strength to networks prepared earlier with di- and tri-telechelic crosslinkers (i.e., $PIB(MA)_2$ and $PIB(MA)_3$, respectively) [4,5]. Scheme 1 shows the structures of the starting materials and the target networks.

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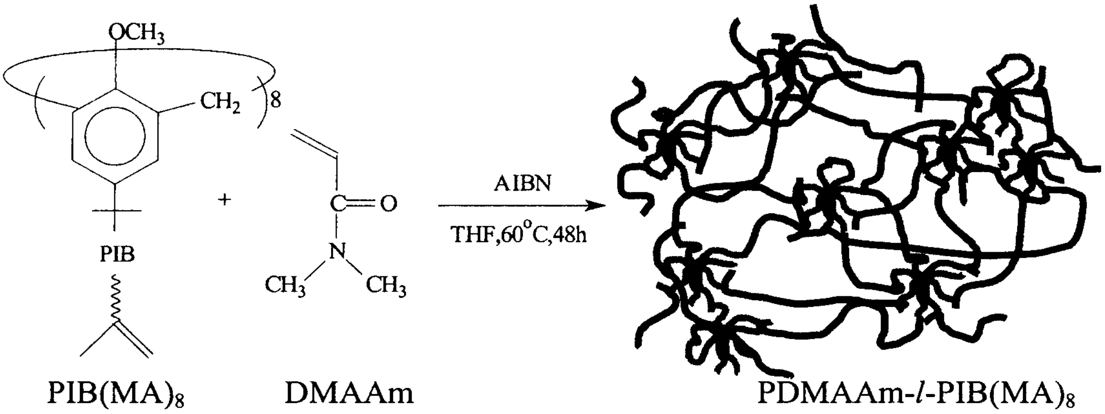
*Part XVII of the series “Amphiphilic Networks.” For XVI of this series see P. Kurian and J. P. Kennedy, J. Polym. Sci., Part A: Polym. Chem., 40, 1209, (2002).



Scheme 1 Synthesis of PDMAAm-*l*-PIB(MA)$_8$ amphiphilic networks

This publication concerns the synthesis of PDMAAm-*l*-PIB(MA)$_8$ networks and their characterization by swelling, soluble fraction (sol), T_g, and mechanical property studies. Findings obtained with networks prepared with octa-functional crosslinking agents were contrasted with those prepared with di- and tri-functional crosslinkers.

Experimental

Materials, Equipment, and Procedures

The source and purification of materials together with the equipment and procedures employed have been described [6-8]. The synthesis and characterization of PDMAAm-*l*-PIB(MA)$_8$ was carried out similarly to networks with PIB(MA)$_2$ and PIB(MA)$_3$ crosslinking agents. [5,7,8].

The molecular weights of the crosslinking agents ($M_{n,PIB}$) were determined by GPC [6] and the M_n of the PDMAAm segments between crosslinking sites ($M_{c,hydrophilic}$) was calculated by [5]:

$$M_{c,hydrophilic} = \frac{W_{PDMAAm} \times M_{n,PIB}}{F \times W_{PIB}} \qquad (1)$$

where W_{PDMAAm} and W_{PIB} are the weight fractions of PDMAAm and PIB in the networks, respectively, and F is the functionality of the crosslinker, that is 8.

Extraction and Swelling

These experiments were carried out on 2.5cm diameter, ~0.45cm thick membranes. Membranes were prepared by charging 0.1g DMAAm, 0.1g PIB(MA)$_8$, and 0.001g AIBN dissolved in 1ml THF into 2.5 cm diameter cylindrical vials, flushing with N_2, sealing them, and maintaining the system for 2 days at 60°C. Samples were Soxhlet extracted sequentially with *n*-hexane and methanol for 24 hours. The percent of sol, S, was determined by:

$$S = \frac{w_{sol}}{w_o} \times 100 \qquad (2)$$

where w_{sol} and w_o are the weights of extracted and starting materials, respectively.

The degree of swelling was determined by swelling membranes in water and *n*-heptane at room temperature until equilibrium [5]. The degree of swelling, d_{sw}, is expressed by [5]:

$$d_{sw} = \frac{w_s - w_d}{w_d} \times 100 \qquad (3)$$

where w_s and w_d are the weights of swollen and dry membranes, respectively. The swelling rates were determined from the initial slopes of degree of swelling versus time traces.

Tg Studies

DSC thermograms were recorded by a DuPont 910 DSC in the -100ºC to 200ºC range with 10ºC/min heating rate. The traces of trapped water were eliminated by repeating the heating/cooling cycle. The T_g's obtained in the second cycle are reported.

Mechanical Properties

In view of the intended use of our membranes (i.e., immunoisolatory tubular devices) the mechanical properties of water-swollen tubular samples have been determined. The preparation of tubules has been described [1,9]. Briefly, copolymerization/crosslinking of DMAAm and various $PIB(MA)_8$'s was carried out in 30cm long, 6-mm diameter glass reactors. Reaction conditions were similar to those described above. Polymer tubules were removed from the glass reactor by multiple water washings and sequentially extracted with *n*-hexane and methanol. Water-swollen tubules had internal diameters of 2-3mm and wall thickness of 200-250μm. Simple extension experiments of 3-4cm long tubules were carried out by the application of force (weights). The weights were applied incrementally to one end of the tubule, while the other end was secured with a clamp. After each step the tubule was allowed to reach equilibrium and the length of the extended tubule was measured. The force was increased incrementally (2-10g) until tubule failure. The engineering stress was obtained by:

$$\sigma = \frac{F}{A_o} \qquad (4)$$

where F is the force and A_o is the initial cross-section. The elastic moduli, E, were obtained from the initial slopes of engineering stress-strain traces (10-15 % strain). Strain was calculated by $\varepsilon = [(l-l_o)/l_o] x100$, where l and l_o are the stretched and initial lengths of the tubule, respectively.

Results and Discussions

We theorized that the crosslinking efficiency of amphiphilic networks could be enhanced by the use of the $PIB(MA)_8$ crosslinking agent and thus we could obtain stronger networks than earlier ones prepared with $PIB(MA)_2$ and $PIB(MA)_3$. Networks synthesized with the latter gave sol fractions in excess of ~5%, which suggests imperfect crosslinking, i.e., the presence of dangling chains and loops. These imperfections, in turn, decrease the mechanical properties.

Table 1 summarizes amphiphilic networks prepared with main chains of PDMAAm crosslinked with PIB(MA)$_8$ (#1-4), PIB(MA)$_3$ (# 5-7), and PIB(MA)$_2$ (# 8-9) crosslinkers. Abbreviations in the second column indicate the main chain (A=PDMAAm), the functionality of the crosslinker (i.e., 8, 3, or 2) followed by the M$_n$x10^{-3} of the crosslinker, the weight % PIB, and the M$_n$ of the PDMAAm segment between crosslinks, M$_{n,hydrophilic}$x10^{-3}. The rest of the column headings are self-explanatory.

Table 1 Synthesis and characterization of amphiphilic networks

#	Network	$M_{n,PIB}$* g/mol (PDI)	$M_{n,Hi}$** g/mol	Mole ratio MA/DMAAm in charge	Sol Fraction, S, %		Degree of Swelling, d_{sw}, (Swelling rate) (d_{sw}/min)	
					nC_6H_{14}	CH_3OH	H_2O	nC_7H_{16}
1	A8-15-50-1.9	15000 (1.08)	1875	0.053	1.41	1.78	1.39 (0.045)	0.63 (0.023)
2	A8-25-50-3.1	25000 (1.11)	3125	0.032	1.64	1.72	1.40 (0.042)	0.70 (0.025)
3	A8-34-50-4.0	34000 (1.09)	4250	0.024	1.8	2.02	1.67 (0.05)	0.76 (0.027)
4	A8-52-50-6.5	52000 (1.17)	6500	0.016	1.88	2.24	1.81 (0.056)	0.86 (0.031)
5	A3-4-50-1.5	4000 (1.12)	1330	0.075	4.25	2.59	0.69	0.42
6	A3-10-50-3.3	10000 (1.1)	3330	0.029	5.10	4.63	0.79	0.6
7	A3-15-50-5.0	15000 (1.08)	5000	0.019	6.35	5.59	0.88	0.6
8	A2-4.5-50-2.2	4500	2250	0.044	6.3	3.5	0.76	0.14
9	A2-9.5-50-4.8	9500	4750	0.021	3.1	6.6	0.81	0.37

*Methacrylate-telechelic crosslinkers: PIB(MA)$_8$, PIB(MA)$_3$ and PIB(MA)$_2$

**$M_{n,hydrophilic}$=$M_{n,PDMAAm}$

The amount of sol fraction (extractables) is a good indication of the extent of crosslinking and less than ~5% sol indicates satisfactory crosslinking [10]. As expected, PIB(MA)$_8$ consistently produced the highest crosslinking efficiency (S<2%) indicating essentially complete incorporation of the starting materials into the networks.

The water-swollen PDMAAm-*l*-PIB(MA)$_8$ networks were consistently opaque suggesting massive phase separation between the incompatible PDMAAm and PIB segments and domains which may arise by intermolecular crosslinking between one or several PIB(MA)$_8$ units. In contrast, networks prepared with PDMAAm and PIB(MA)$_3$ or PIB(MA)$_2$ were optically clear, and TEM showed a co-continuous salt-pepper morphology with domain diameters in the 20-50Å range [11].

The equilibrium degree of swelling and swelling rates of various membranes in water and *n*-heptane were investigated. According to the data summarized in Table 1, the swelling of PDMAAm-*l*-PIB(MA)$_8$ in both water and *n*-heptane is significantly higher than those of membranes crosslinked by PIB(MA)$_3$ and PIB(MA)$_2$. The swelling in water of PDMAAm-*l*-PIB(MA)$_8$ is at least double that of the other networks even with comparable M$_{c,\ hydrophilic}$.

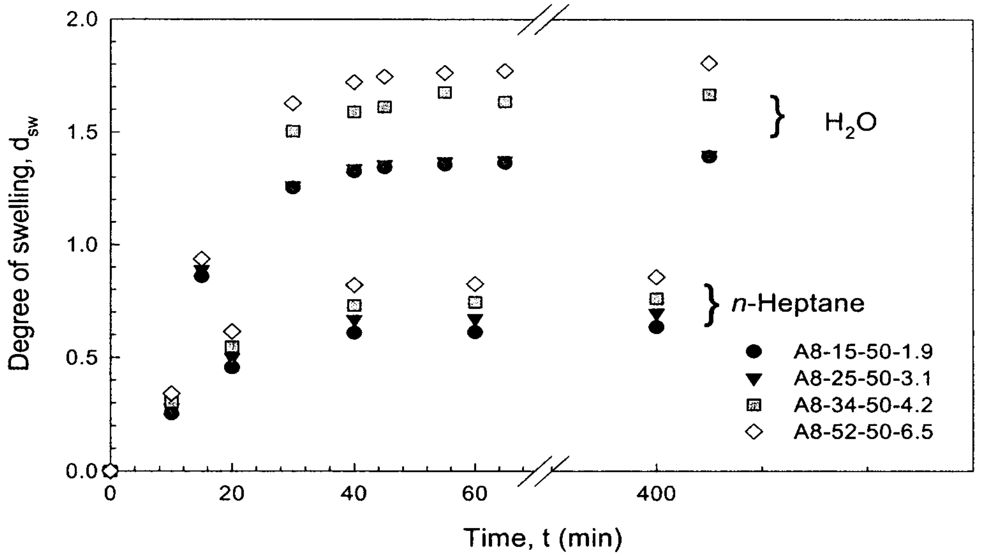


Figure 1 Swelling of PDMAAm-*l*-PIB(MA)$_8$ amphiphilic networks in water and *n*-heptane.

Figure 1 shows the rates and equilibrium swelling as a function of time. The rates of swelling of PDMAAm-*l*-PIB(MA)$_8$ in both water and *n*-heptane were found to be much higher (equilibrium swelling reached in 1hour) than of compositionally similar other membranes (e.g., equilibrium swelling of PDMAAm-*l*-PIB(MA)$_2$ reached in both solvents in ~10 hours [8]; swelling data of PDMAAm-*l*-PIB(MA)$_3$ see [5]). High and rapid swelling are desirable to facilitate material transport through membranes for immunoisolatory applications.

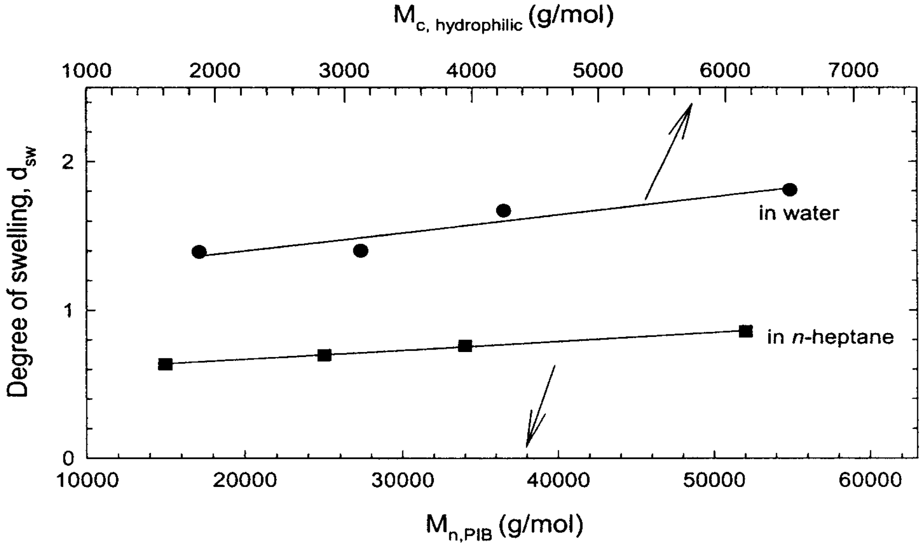


Figure 2 Effect of $M_{c,hydrophilic}$ and $M_{n,PIB}$ on equilibrium swelling of PDMAAm-*l*-PIB(MA)$_8$ amphiphilic networks.

Figure 2 shows equilibrium swelling in both water and *n*-heptane as a function of $M_{c,hydrophilic}$ and $M_{n,PIB}$. As anticipated, swelling increases with $M_{c,hydrophilic}$ in water, and with $M_{n,PIB}$ in *n*-heptane.

Figure 3 shows DSC traces of two representative membranes. The T_g's at –64°C and 100°C indicate phase separated PIB and PDMAAm domains, respectively. The traces also show a T_g at ~ -7°C that suggests an interphase. The latter transition is probably not due to water because it persisted in DSC traces obtained with samples cycled to 200°C three times.

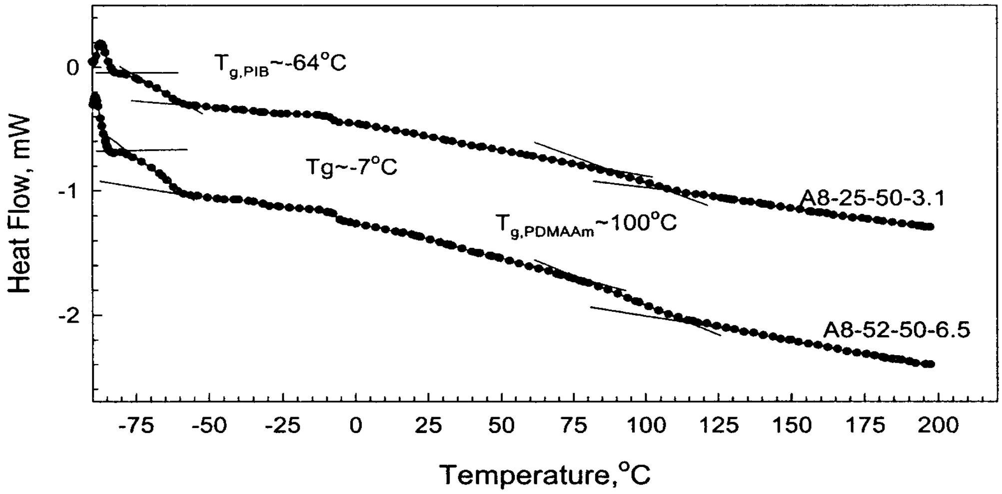


Figure 3 DSC thermograms obtained upon heating of PDMAAm-*l*-PIB(MA)$_8$ networks from –100°C to 200°C at 10°C/min.

Table 2 shows engineering stress, elastic modulus and elongation of representative water-swollen tubular membranes. The water-swollen tubules are rubbery with elongations in the 200-260% range, and stresses at break in the 0.4-0.58MPa range. Contrary to expectations, the overall mechanical properties of the PDMAAm-*l*-PIB(MA)$_8$ did not increase significantly with crosslinking efficiency, most likely due to the presence of the large phase-separated domains [12,13].

Table 2 Mechanical properties of water-swollen amphiphilic tubules.

#	Network	Eng. Stress, σ, MPa	Elastic Modulus, E, MPa	Elongation, ε, %
1	A8-15-50-1.9	0.58±0.1	1.03±0.24	260±129
2	A8-25-50-3.1	0.56±0.13	0.89±0.09	208±39
4	A8-52-50-6.5	0.40±0.46	0.6±0.12	249±105
5	A3-4-50-1.5	0.42±0.2	1.6±0.28	51±5
6	A3-10-50-3.3	0.50±0.27	0.92±0.21	187±46
7	A3-15-50-5.0	0.49±0.08	0.71±0.17	263±29
8	A2-4.5-50-2.2	0.29±0.31	0.82±0.23	59±69

Figures 4a and 4b show stress-strain traces of membranes crosslinked by PIB(MA)$_8$ and PIB(MA)$_3$, respectively and the effect of crosslinker molecular weight on the stress-strain behavior. Although we expected superior mechanical properties for PDMAAm-*l*-PIB(MA)$_8$, according to these data the overall properties of the two families of networks are not much different. We suspect that the absence of a discernible effect of the octa-functional crosslinker is due to synthetic deficiencies giving rise to massive network imperfections, i.e., intramolecular crosslinking between PIB(MA)$_8$ units leading to overly large heterophases [12,13].

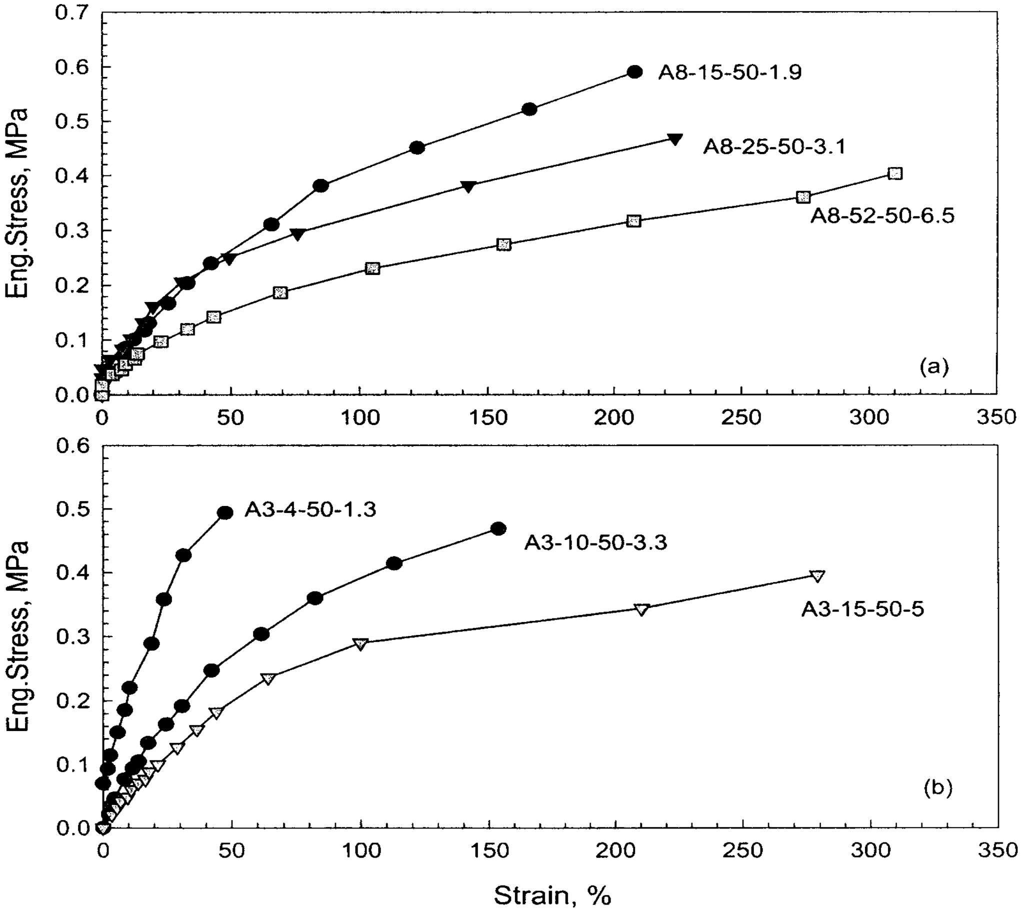


Figure 4 Stress-strain behavior of water-swollen tubules synthesized by the use of different molecular weight PIB(MA)$_8$ (a) and PIB(MA)$_3$ (b) crosslinkers.

Conclusions

Novel amphiphilic networks were synthesized by copolymerization/ crosslinking of PDMAAm and PIB(MA)$_8$. Crosslinking efficiency was essentially 100%. The networks exhibited relatively high (130-180%) swelling in water. Water-swollen networks were rubbery with elongations in the 200-260% range and stresses at break in the 0.4-0.58MPa range. Evidently, the mechanical and physical properties of PDMAAm-*l*-PIB(MA)$_8$ membranes are sufficient for immunoisolatory applications.

Acknowledgements

The authors thank the National Science Foundation, Grant 9988808 and SUMMA Health System for financial support.

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