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Amphiphilic Networks. I. Network Synthesis by Copolymerization of Methacryloyl-Capped Polyisobutylene with 2-(Dimethylamino) Ethyl Methacrylate and Characterization of The Networks

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AMPHIPHILIC NETWORKS. I. NETWORK SYNTHESIS BY COPOLYMERIZATION OF METHACRYLOYL-CAPPED POLYISOBUTYLENE WITH 2-(DIMETHYLAMINO)ETHYL METHACRYLATE AND CHARACTERIZATION OF THE NETWORKS

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ABSTRACT

New amphiphilic networks have been synthesized by free-radical copolymerization of hydrophobic methacryloyl-capped polyisobutylenes (MA-PIB-MA) with hydrophilic 2-(dimethylamino)ethyl methacrylate. Two MA-PIB-MAs have been prepared with $\bar{M}_n$ = 4920 and 10 200, and two series of networks were prepared with MA-PIB-MA contents between 48 and 71.5%. Variation of the molecular weight of MA-PIB-MA and its concentration in the network allows for a wide range of mechanical properties and swellability in hydrophilic and hydrophobic solvents. Differential scanning calorimetry shows the existence of two glass transitions in these networks and thus indicates a phase-separated domain structure. Tensile strengths and elongations were dependent on MA-PIB-MA contents varying from 57.7 to 39.8 kg/cm^2 and from 168 to 200%, respectively, with increasing MA-PIB-MA content. Solvent swelling of the networks ranged from 170 to 20% in water and from 40 to 170% in *n*-heptane with increasing MA-PIB-MA contents.

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INTRODUCTION

An amphiphilic network is a random assemblage of hydrophilic and hydrophobic chains that is able to swell in both water and hydrocarbons. As these materials swell in water, they fall under the general classification of hydrogels or water-swellable networks. Since Wichterle and Lim proposed the use of hydrogels for biomedical applications in 1960 [1], hydrogels have been extensively studied and used for a number of biomedical applications [4, 5], controlled drug release [6, 7], enzyme immobilization [8, 9], blood-contacting applications [10, 11], and other uses [12, 13]. The efficacy of hydrogels as biomaterials results from the similarity of their hydrated structure to natural tissue.

Although hydrogels of extremely diverse chemical composition have been prepared [14-18], there are only very few examples of the preparation of amphiphilic networks [19-21], probably due to synthetic difficulties.

The amphiphilic network described in this paper is a structurally novel two-component system. Figure 1 shows a schematic representation of this type of network. In such a network, hydrophilic chains are connected to hydrophobic

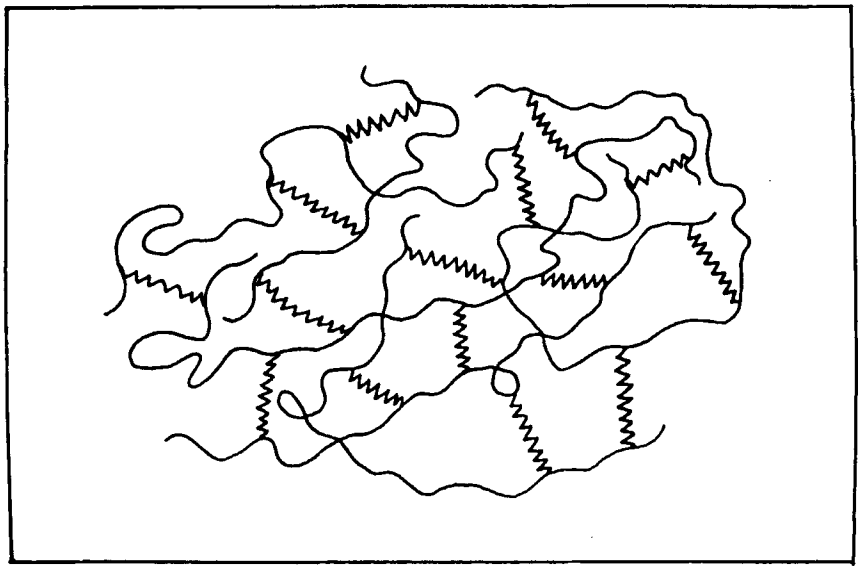

FIG. 1. An idealized representation of the amphiphilic network.

chains at trifunctional crosslink points. Because of the difference in chemical structure of these chains, they should be thermodynamically incompatible and thus exhibit microphase separation.

The networks that we have prepared contain poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) as the hydrophilic component and methacryloyl-capped polyisobutylene (MA-PIB-MA) as the hydrophobic component. The synthesis of MA-PIB-MA has been reported [22]. The methacrylate capping groups in the MA-PIB-MA telechelic macromer are readily copolymerizable under conventional free-radical conditions with DMAEMA due to the similarity between the structures of the methacrylate end groups in the two ingredients, and the resulting materials should be randomly crosslinked networks. Variation of the molecular weight of MA-PIB-MA and its concentration in the network allows for a wide range of solvent swellability and other properties.

EXPERIMENTAL

Materials

The synthesis and purification of MA-PIB-MA has been described [22]. 2-(Dimethylamino)ethyl methacrylate (Aldrich Chemical Co.) was used without further purification. Azoisobutyronitrile (AIBN) was recrystallized from methanol. THF was distilled over calcium hydride. *n*-Heptane (reagent grade) was used without further purification.

Techniques

Molecular weights were determined by a Waters Associates high-pressure GPC instrument (Model 6000 A Pump, WISP 710 B automatic injector, a series of five μ-Styragel columns (10^5, 10^4, 10^3, 500, and 100 Å), differential refractometer 2401, and UV absorbance detector 440), and a calibration curve was made by using well-fractionated polyisobutylene standards. Due to the insoluble nature of the network, quantitative compositional analysis was done with an FTIR spectrometer equipped with an attenuated total reflectance (ATR) attachment. The FTIR spectra were obtained using a Beckman FT 2100 spectrometer equipped with a Spectra Tech Model 300 ATR attachment. ATR spectra were run with a 50-mm KRS-5 crystal at a 45° angle. DSC analysis was carried out on a Du Pont 1090 thermal analyzer under nitrogen at a 20°C/min heating rate. Stress-strain data were obtained on an Instron universal testing instrument with a 5-kg load cell and 5 cm/min crosshead speed at room temperature with microdumbbell samples.

Network Synthesis

The networks were prepared in film and cube shapes. In the case of film, the copolymerization of MA-PIB-MA with DMEAMA was carried out in 1-ounce cylindrical bottles with AIBN initiator and THF solvent at 60°C. Before the system gelled and became unpourable, the mixture was transferred to an aluminum dish which was then placed in an oven protected with nitrogen at 60°C for 3 d to give a film with a thickness of about 1 mm. It is important to judge the time accurately before transferring the charge to the aluminum dish in order to obtain good films. Early transfer will result in phase separation during film formation. In the case of the cube, the polymerizing charge was kept in the cylindrical bottle for 3 d and was then cut into cubes with ~ 6 mm sides.

To remove unreacted MA-PIB-MA, unreacted DMAEMA, and PDMAEMA homopolymer, the network was extracted sequentially with *n*-hexane for 24 h, ethanol for 5 h, and H_2O for 2 d.

Swelling Experiment

The dried and weighed network was placed in solvent (distilled water or *n*-heptane) and then weighed periodically until constant weight was reached. The swelling curve was obtained by plotting the amount of solvent absorbed per gram network (S/N) against time.

RESULTS AND DISCUSSION

Table 1 shows characteristics of the MA-PIB-MA prepolymers used in network synthesis, and Table 2 details copolymerization conditions, quantities extracted, and network characteristics. Two series of networks were prepared. The network abbreviation code indicates the $\bar{M}_n$ of the starting MA-PIB-MA (rounded to the closest thousand and divided by 1000) and the percent of PIB in the network. For example, N-5-48 indicates a network prepared with $\bar{M}_n$ 4920 MA-PIB-MA containing 48.5% PIB.

The copolymerization of MA-PIB-MA with DMAEMA and the resulting network may be schematized as shown in Fig. 2.

The copolymer network contains PIB and PDMAEMA sequences. Since the polymerizable MA end groups of the MA-PIB-MA and DMAEMA are identical, the two sequences are expected to be connected in a random manner. As shown in Fig. 2, the network is expected to have average molecular weights between crosslinks, $\bar{M}_c$, and $\bar{M}_{c,\mathrm{PIB}}$ should be identical to $\bar{M}_n$ of

TABLE 1. Molecular Characteristics of MA-PIB-MAs Used for Network Synthesis

	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{F}_n$[a] NMR	$\bar{F}_n$[a] FTIR
N-5	4 920	1.6	1.99	2.27 (± 0.2)
N-10	10 200	1.7	2.0	2.0 (± 0.2)

[a]Number-average terminal functionality determined spectroscopically.

the MA-PIB-MA. The value of $\bar{M}_{c,\mathrm{PDMAEMA}}$ may be estimated by knowing the overall composition of the network, the $\bar{M}_n$ of the MA-PIB-MA, and assuming complete incorporation of the MA-PIB-MA in the network. Estimated $\bar{M}_{c,\mathrm{PDMAEMA}}$ values are listed in the last column of Table 2.

The overall composition of the networks prepared by copolymerization of MA-PIB-MA with DMAEMA was determined by FTIR spectroscopy. A doublet at 1362 and 1400 cm^{-1}, due to *gem*–CH_3 groups in MA-PIB-MA, was used to quantify the MA-PIB-MA in the network. An absorption at 2772 cm^{-1}, due to the $-CH_2-$ stretching vibration in the tertiary amine, was used to

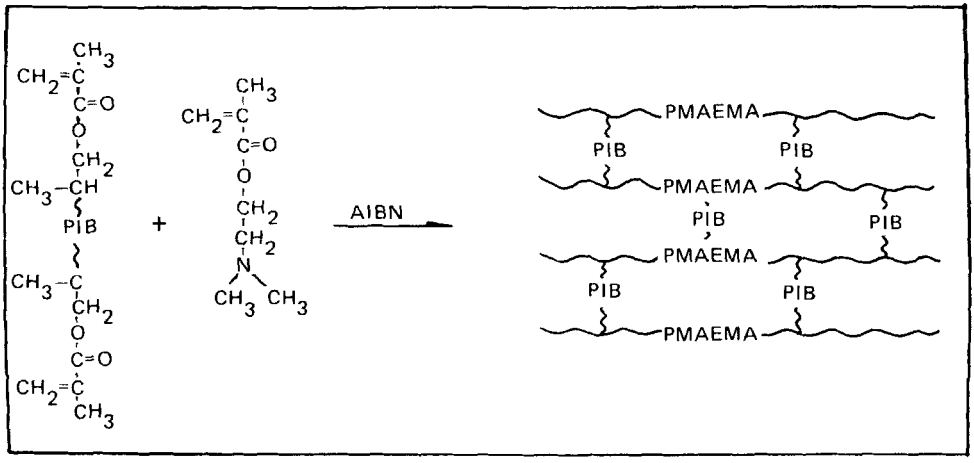

FIG. 2. Copolymerization of MA-PIB-MA with DMAEMA and the resulting network.

TABLE 2. Network Synthesis Conditions and Compositions[a]

Network	Charge		Extract, %	Network characteristics	
	MA-PIB-MA, g	DMAEMA, g		PIB, %	$\bar{M}_{c,\text{PDMAEMA}}$[b]
N-5-48	0.6	1.4	21.4	48.5	2610
N-5-51	0.8	1.2	26.5	51.0	2360
N-5-53	1.0	1.0	27.1	53.0	2180
N-5-61	1.2	0.8	29.3	61.0	1570
N-5-64	1.4	0.6	30.5	64.0	1380
N-10-49	0.6	1.4	20.7	49.5	5190
N-10-53	0.8	1.2	22.4	53.0	4700
N-10-56	1.0	1.0	23.8	56.3	3950
N-10-58	1.2	0.8	27.3	58.2	3660
N-10-71	1.4	0.6	35.7	71.5	2030

[a]Copolymerizations in 7 mL THF with 0.07 g AIBN at 60°C.
[b]Calculated; for assumptions, see text.

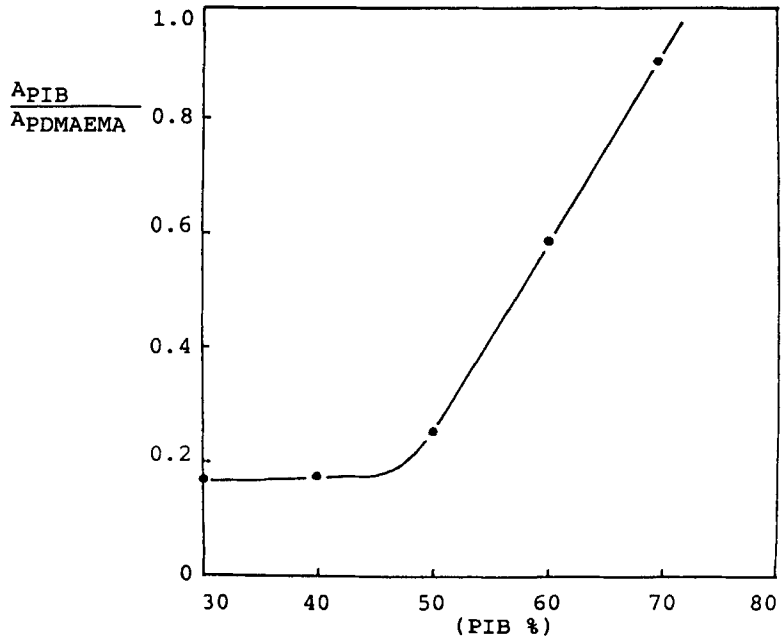

FIG. 3. FTIR calibration curve for the amphiphilic network.

quantify the PDMAEMA content in the network. To obtain the calibration curve for determining overall network composition, a series of unextracted networks was prepared and the overall compositions were determined from their FTIR absorbances at 1362, 1400, and 2772 cm^{-1}. Unextracted networks must be used to ensure that true overall network compositions are obtained for calibration purposes (i.e., the FTIR absorptions of *gem*-CH_3 groups in MA-PIB-MA and that of $-CH_2-$ in the *t*-amine should be the same in the network, homopolymer, and unreacted monomer). The calibration curve was obtained by plotting the ratio of these absorbances against the MA-PIB-MA content of the networks. Figure 3 shows the calibration curve constructed in this manner. The percent PIB in an unknown network can be obtained from the FTIR spectrum by determining the absorbances and using the calibration curve. The results in Table 2 were obtained in this manner. The sensitivity of this technique is very good at high PIB contents; however, below about 47% PIB in the network, the sensitivity of this technique is unsatisfactory.

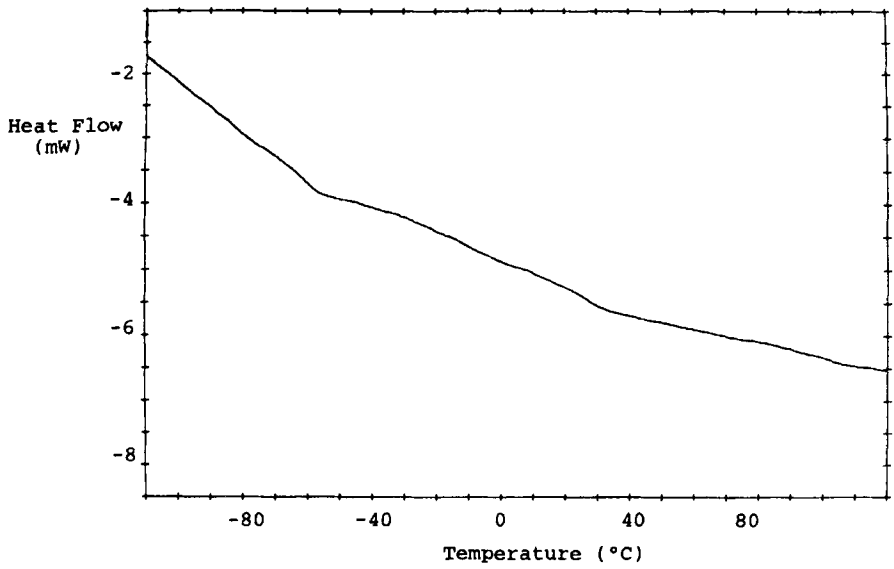

FIG. 4. DSC trace of the amphiphilic network N-10-56.

Figure 4 shows the DSC trace of a representative network (N-10-56). The trace exhibits two T_g's, one at -60°C and one at 30°C, indicating phase segregation into PIB (T_g -73°C) [23] and PDMEMA domains (T_g 19°C) [23]. The higher-than-literature T_g values may be due to the relatively fast rate of heating used in our measurements (20°C/min) or to the restricted motion of the network chain segments. (We thank the referee for the latter suggestion.)

Mechanical properties of select samples were investigated. Figure 5 shows stress-strain traces of representative dry networks. Drying was performed in an oven at 60°C under a nitrogen atmosphere for 25 h. The tensile strengths increase with increasing PDMAEMA content. Plastic deformation and yielding also increase with increasing PDMAEMA content, which may be due to lower crosslink density and/or to phase segregation, PDMAEMA having become the continuous phase. Elongations decrease with increasing PDMAEMA, probably for the same reasons.

Figures 6 and 7 show network swelling curves (film, 1 mm thick) in water. Despite composition and MA-PIB-MA molecular weight variations, swelling of the networks reached maxima in less than ~3 h. However, the degree of swelling changes significantly with changes in network composition and the $\bar{M}_n$ of

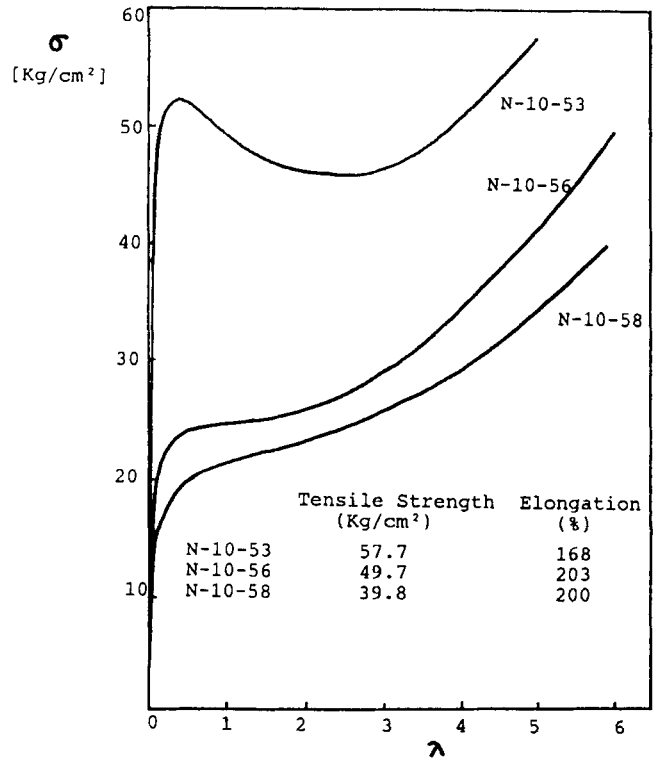

FIG. 5. Stress-strain curves of amphiphilic networks.

the MA-PIB-MA. Thus the degree of swelling in water decreases with increasing PIB content, e.g., swelling decreases from 170 to 30% by increasing the PIB content from 49.5 to 71.5%. Not too surprisingly, the degree of swelling in water increases with increasing $\bar{M}_n$ of MA-PIB-MA in the network. Evidently by decreasing the degree of crosslinking, the degree of swelling increases.

Figures 8 and 9 show swelling curves by the use of *n*-heptane. Unlike swelling in water, the time needed to reach maximum swelling is composition-dependent. At higher PIB contents the swelling in *n*-heptane is rather fast (with 71.5% PIB, swelling reaches a maximum in 100 min). At lower PIB contents, swelling in *n*-heptane is slower and linear for ~200 min. Similar to the swelling in water, the degree of swelling in *n*-heptane charges with network composition and $\bar{M}_n$ of PIB.

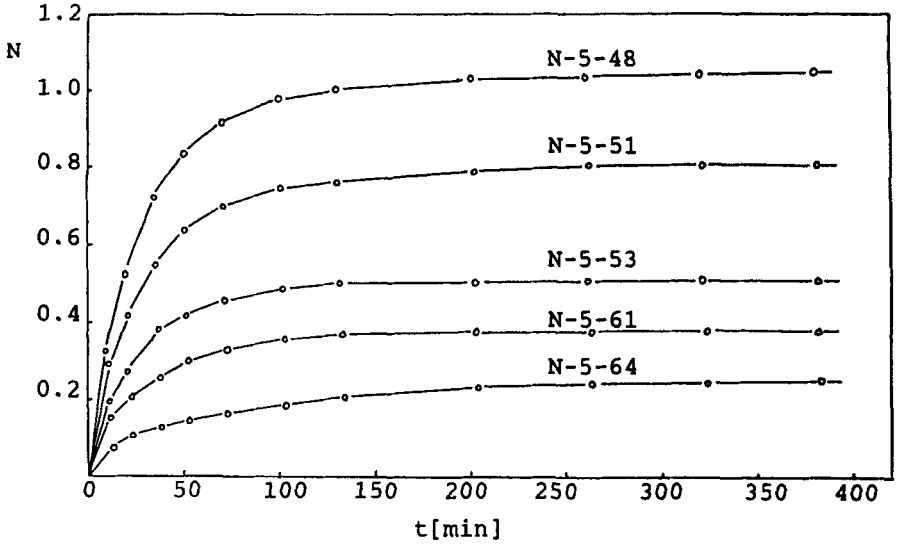

FIG. 6. Swelling of amphiphilic networks in water (room temperature).

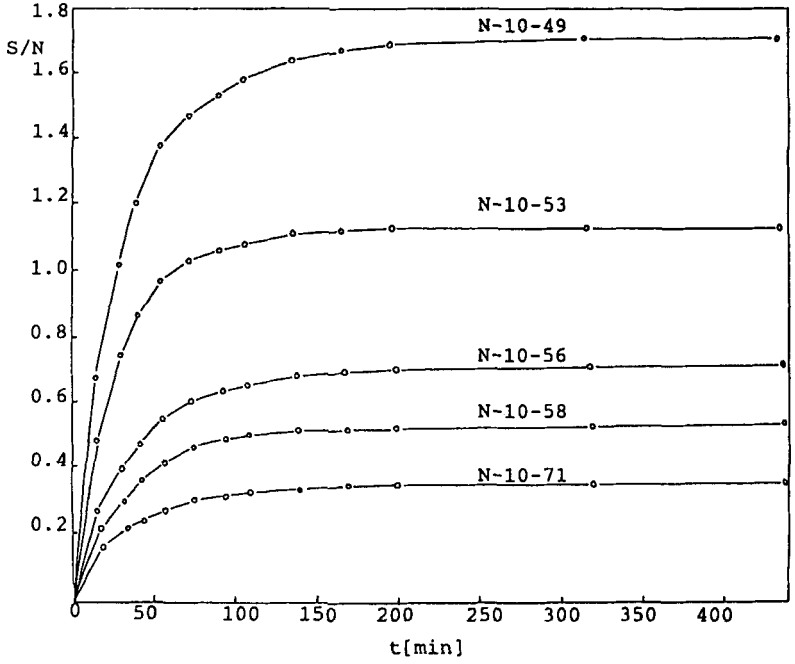

FIG. 7. Swelling of amphiphilic networks in water (room temperature).

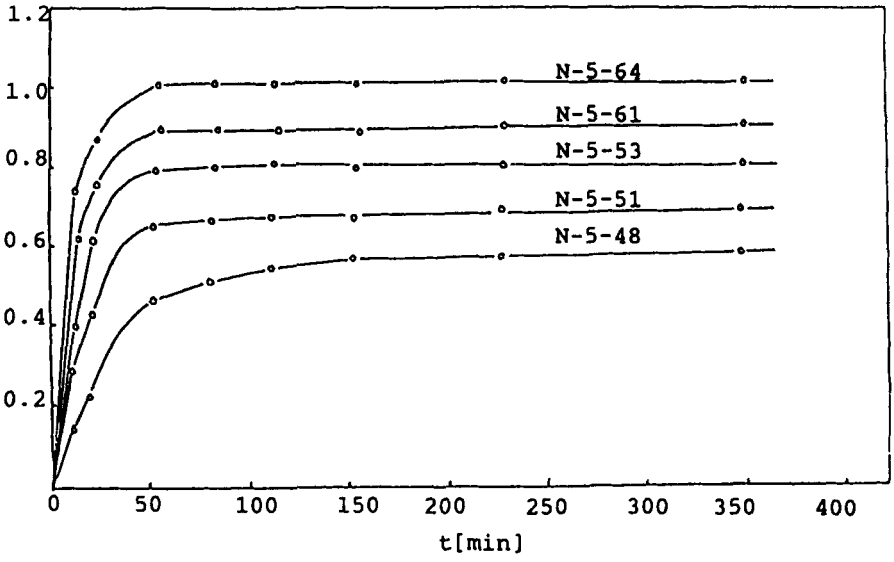

FIG. 8. Swelling of amphiphilic networks in heptane (room temperature).

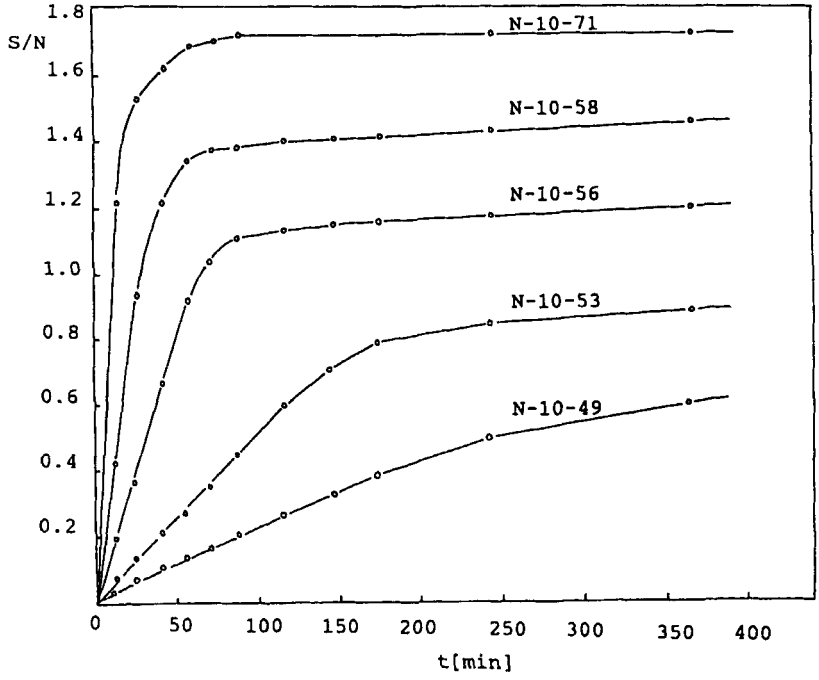

FIG. 9. Swelling of amphiphilic networks in heptane (room temperature).

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