Novel Amphiphilic Network Polymers Consisting of Short Primary Polymer Chains and Long Crosslink Units with Opposite Polarities Obtained by Free-Radical Crosslinking Monomethacrylate/Dimethacrylate Copolymerizations

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We have been concerned with the mechanistic discussion of 3-dimensional network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds with the aim to molecularly design vinyl-type network polymers with high performance and high functionality.[1] As an extension of our continuing studies, we have discussed the preparation of novel amphiphilic network polymers obtained by free-radical crosslinking monovinyl/divinyl copolymerizations.[2,3] The present work deals with the amphiphilic network polymers consisting of short primary polymer chains and long crosslink units with opposite polarities.[4] Solution copolymerizations of benzyl methacrylate (BzMA) or 2-hydroxyethyl methacrylate (HEMA) with 5 mol % of tricosaethylene glycol dimethacrylate (PEGDMA-23) or heneicosapropylene glycol dimethacrylate (PPGDMA-21), respectively, were carried out in the presence of different amounts of lauryl mercaptan (LM) as a chain transfer agent (Fig. 1). The vinyl-type network polymers formed via highly branched prepolymers have abundant dangling chains as their characteristic feature, especially when the primary polymer chain length is short, because both terminal parts of primary polymer chain would be dangling chains. The amphiphilicity of the resulting gels was checked by measuring their swelling ratios in the mixed solvents with opposite polarities. For example, we attempted to measure their swelling ratios of resulting amphiphilic poly(HEMA-*co*-PPGDMA-21) gels in the mixed solvents consisting of nonpolar *t*-butylbenzene (*t*-BB) and polar MeOH; thus, with an increase in the vol % of MeOH, the gels shrank to the smallest swelling ratio at the start point (i.e., in pure *t*-BB), swelled gradually and then rather sharply beyond 20 vol %, reached the maximum swelling at about 70 vol %, and then shrank gradually up to a rather high swelling ratio at the terminal (i.e., in pure MeOH) (Fig. 2). The profiles of the solvent component dependencies of the swelling ratios are characteristic of novel amphiphilic gels. The influence of H_2O on the characteristic swelling behavior of resulting amphiphilic gels was examined by measuring their swelling ratios in the mixed solvents consisting of MeOH/H_2O, acetone/H_2O, or dioxane/H_2O. Furthermore, the response of swelling/deswelling equilibrium of the resulting amphiphilic lipogels was checked by changing the solvent polarity. Also, we tried to examine the influence of physical interactions on the crosslinking reactions with the aim to control the network formation and molecularly design amphiphilic vinyl-type network polymers.

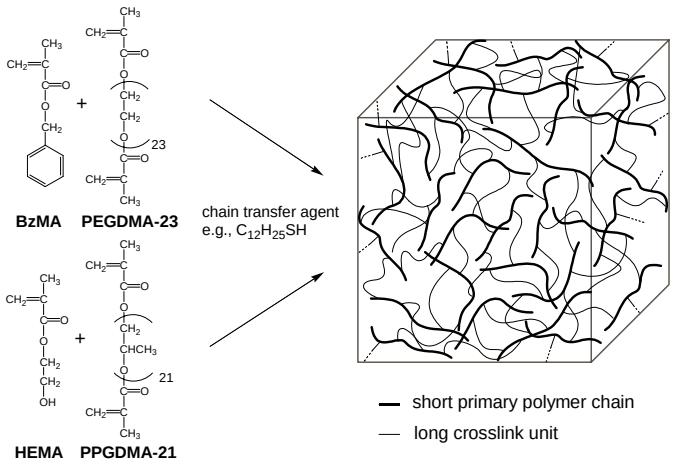

Fig. 1 A schematic picture of amphiphilic vinyl-type network polymer consisting of short primary polymer chains and long crosslink units with opposite polarities.

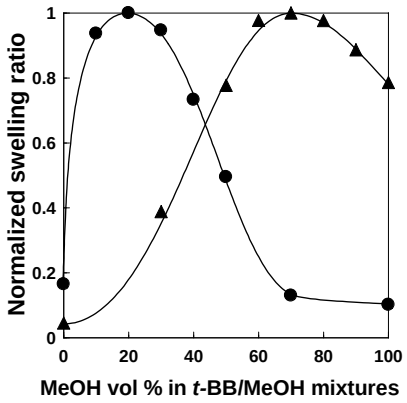

Fig. 2 Correlations of the swelling ratios of resulting gels in the mixed solvents for (J) poly(BzMA-*co*-PEGDMA-23) and (H) poly(HEMA-*co*-PPGDMA-21) gels.
BzMA/PEGDMA-23 (95/5) copolymerizations
(In dioxane, dilution 2/3, [AIBN] = 0.04 mol/L, 50 °C, [LM]/[total monomer] = 1/20)
HEMA/PPGDMA-21 (95/5) copolymerizations
(In MeOH, dilution 2/3, [AIBN] = 0.04 mol/L, 50 °C, [LM]/[total monomer] = 1/20)

References:
(1) Matsumoto, A. *Adv. Polym. Sci.* **1995**, *123*, 41.
(2) Matsumoto, A. et al. *Eur. Polym. J.* **2001**, *37*, 135.
(3) Matsumoto, A. et al. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4396.
(4) Doura, M. et al. *Macromolecules*, in press.

Novel Amphiphilic Network Polymers Consisting of Short Primary Polymer Chains and Long Crosslink Units with Opposite Polarities Obtained by Free-Radical Crosslinking Monomethacrylate/Dimethacrylate Copolymerizations

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Introduction

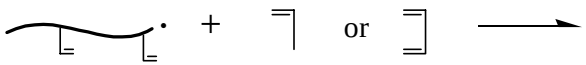
We have been concerned with the mechanistic discussion of the 3-dimensional network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds.

Research goal

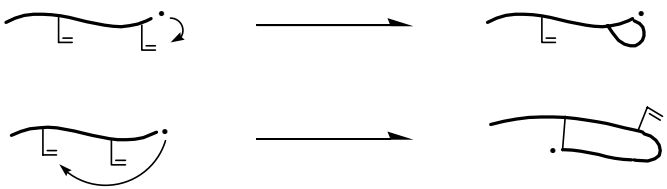
Molecular-design of vinyl-type network polymers with high performance and high functionality: 1) Elucidation of the crosslinking reaction mechanism, 2) Control of network formation.

A reaction scheme for the network formation processes in the free-radical crosslinking monovinyl/divinyl copolymerization

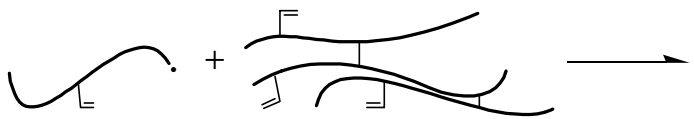
1) Intermolecular propagation with monomer:



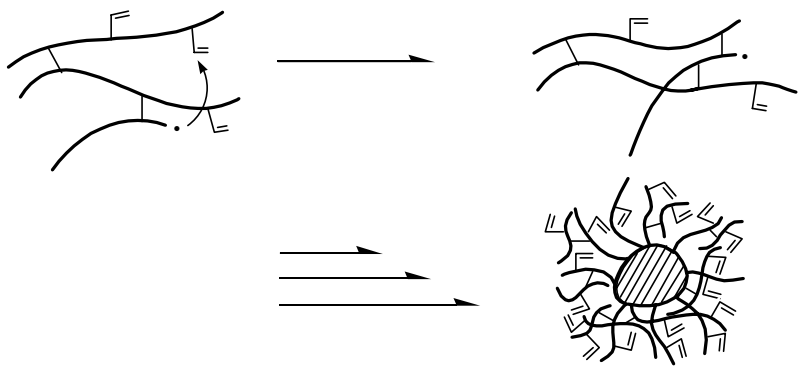
2) Intramolecular cyclization:



3) Intermolecular crosslinking with prepolymer:

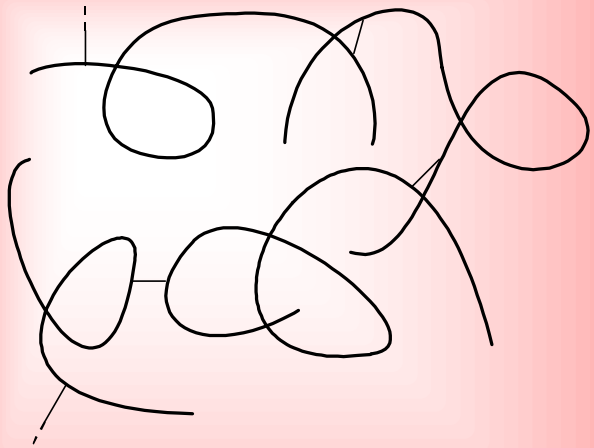


4) Intramolecular crosslinking:

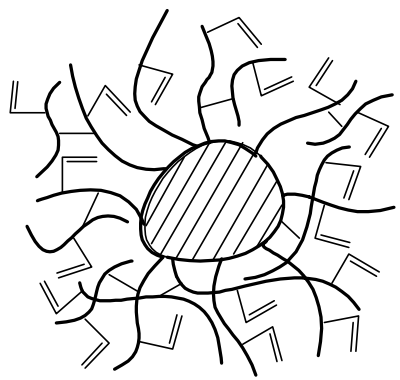


(Microgel)

Two extreme structures of crosslinked polymers



(A) Ideal network polymer



(B) Microgel

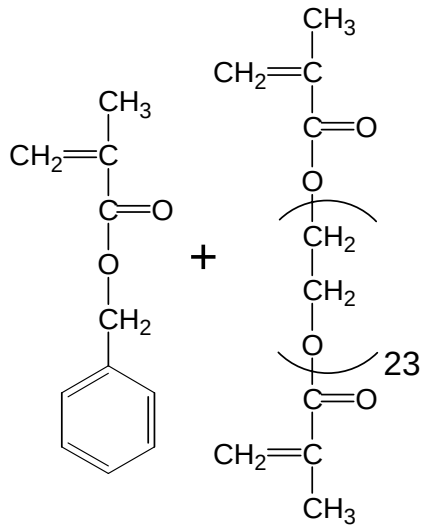
Outline

1. Synthesis and characterization of novel amphiphilic network polymers consisting of **short** primary polymer chains and **long** crosslink units with opposite polarities obtained by free-radical crosslinking monomethacrylate/dimethacrylate copolymerizations

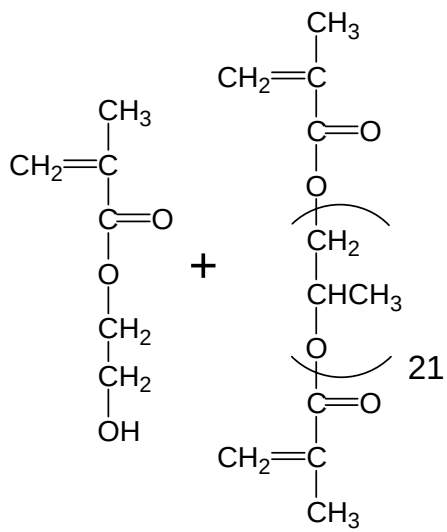
2. Control of deswelling rate of amphiphilic lipogels by the aid of dangling chains

3. Controlled network formation in free-radical crosslinking monomethacrylate/dimethacrylate copolymerizations by amphiphilic nature of short primary polymer chains and long crosslink units with opposite polarities

Schematic picture of amphiphilic vinyl-type network polymer consisting of **short** primary polymer chains and **long** crosslink units with opposite polarities

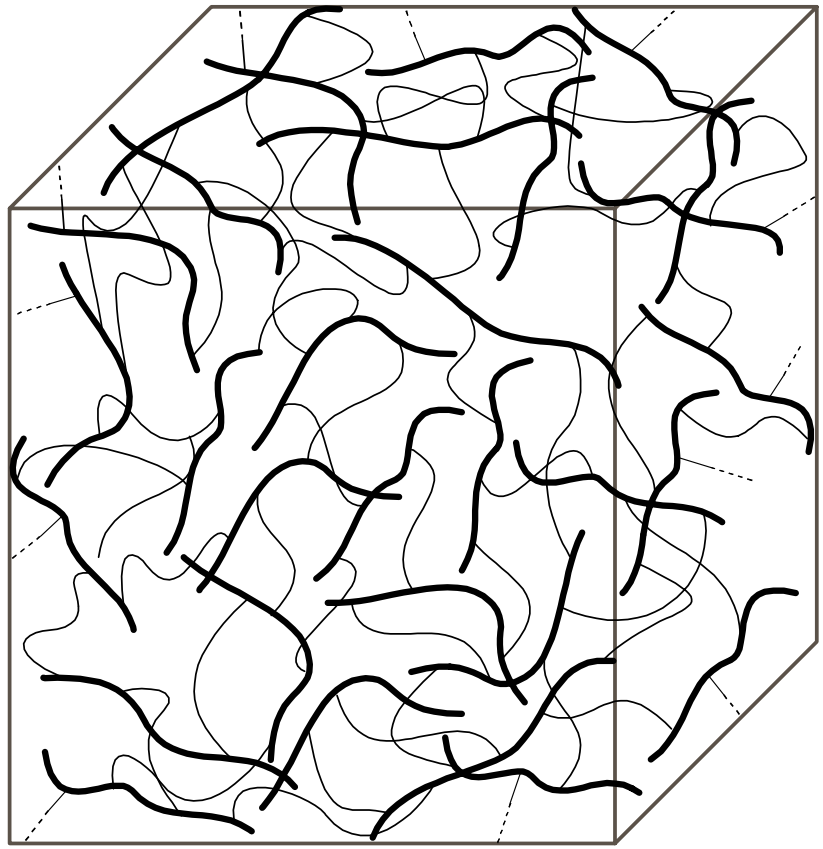


BzMA **PEGDMA-23**



HEMA **PPGDMA-21**

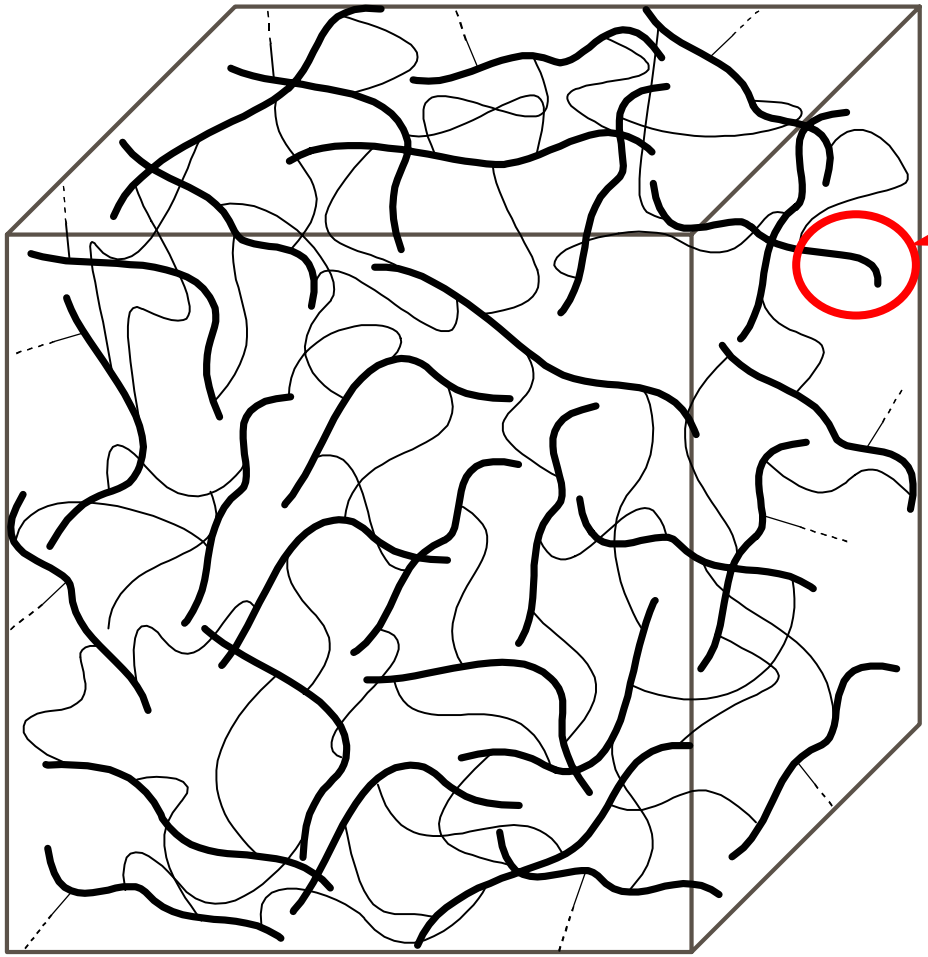
chain transfer agent
e.g., $C_{12}H_{25}SH$



short primary polymer chain

long crosslink unit

Influence of primary polymer chain length on the swelling behavior of resulting amphiphilic gels



dangling chain

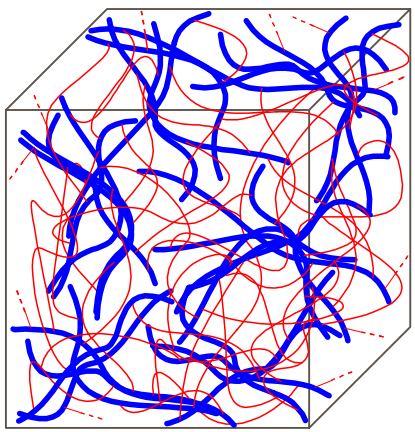
When the primary polymer chain length is short, the vinyl-type network polymers have abundant dangling chains, because both terminal parts of primary polymer chain would be dangling chains.

The dangling chains would have a significant influence on the swelling behavior of the resulting gels because of their active segmental motions.

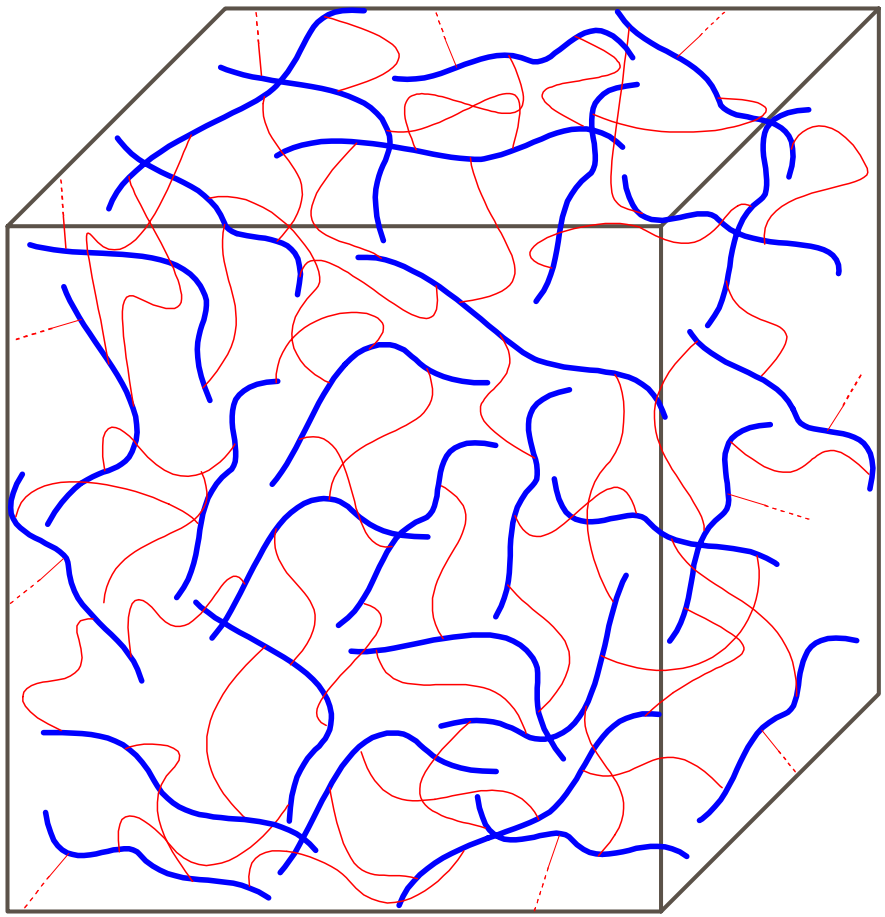
— short primary polymer chain

— long crosslink unit

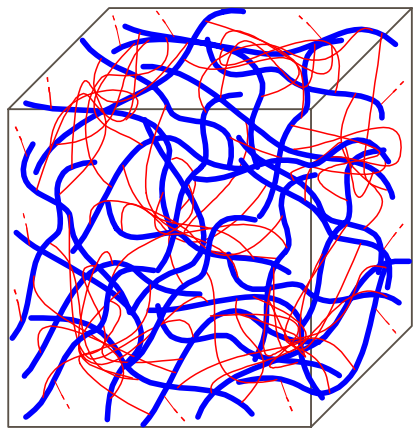
Three typical conformations of network segments of amphiphilic gel consisting of **short** primary polymer chains and **long** crosslink units with opposite polarities



(A) Assembly of short primary polymer chains



(B) No assembly of both primary polymer chains and crosslink units



(C) Assembly of long crosslink units

Comparison of actual and theoretical gel points in the copolymerizations of HEMA with 5 mol% of PPGDMA-21 in the presence of different amounts of lauryl mercaptan (LM)

[LM]/ [total monomer]	$\bar{P}_{w,0}$ [b]	gel point (%)		actual gel point[e]/ theor gel point[c]
		theor[c]	actual[d]	
1/100	**416**	**2.5**	**25.1 (18.5)[e]**	**7.3**
1/50	**257**	**4.1**	**34.3 (25.3)[e]**	**6.2**
1/20	**113**	**9.4**	**63.2 (46.6)[e]**	**5.0**

[a] In MeOH, dilution 2/3, [AIBN] = 0.04 mol/L, 50 °C.

[b] Estimated by LS measurement.

[c] Theoretical gel point: $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$.

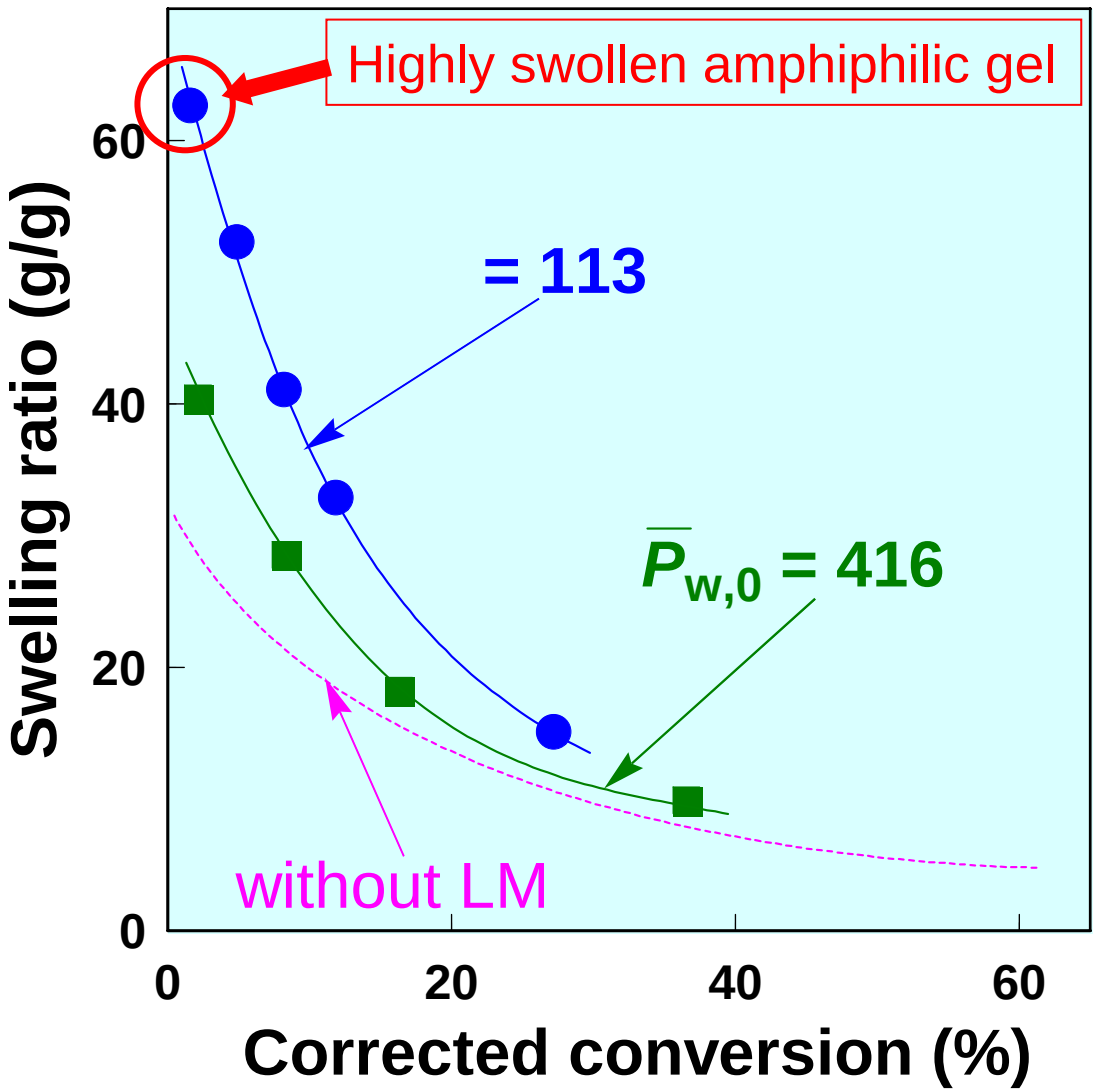
[d] Obtained on monomer basis.

[e] Obtained as the vinyl group conversion calculated by assuming equal reactivity of HEMA and PPGDMA-21 vinyl groups.

The formation of a polar growing polymer radical by the incorporation of HEMA unit would reduce the occurrence of intermolecular crosslinking reaction with unreacted methacrylic double bonds present at the terminal of a nonpolar poly(oxypropylene) chain. Therefore, despite the delayed gelation from FS theory, the homogeneous network formation was expected.

Decrease in swelling ratios of resulting gels in THF with the progress of polymerization beyond the gel point in the presence of LM

HEMA/PPGDMA-21 (95/5) copolymerizations

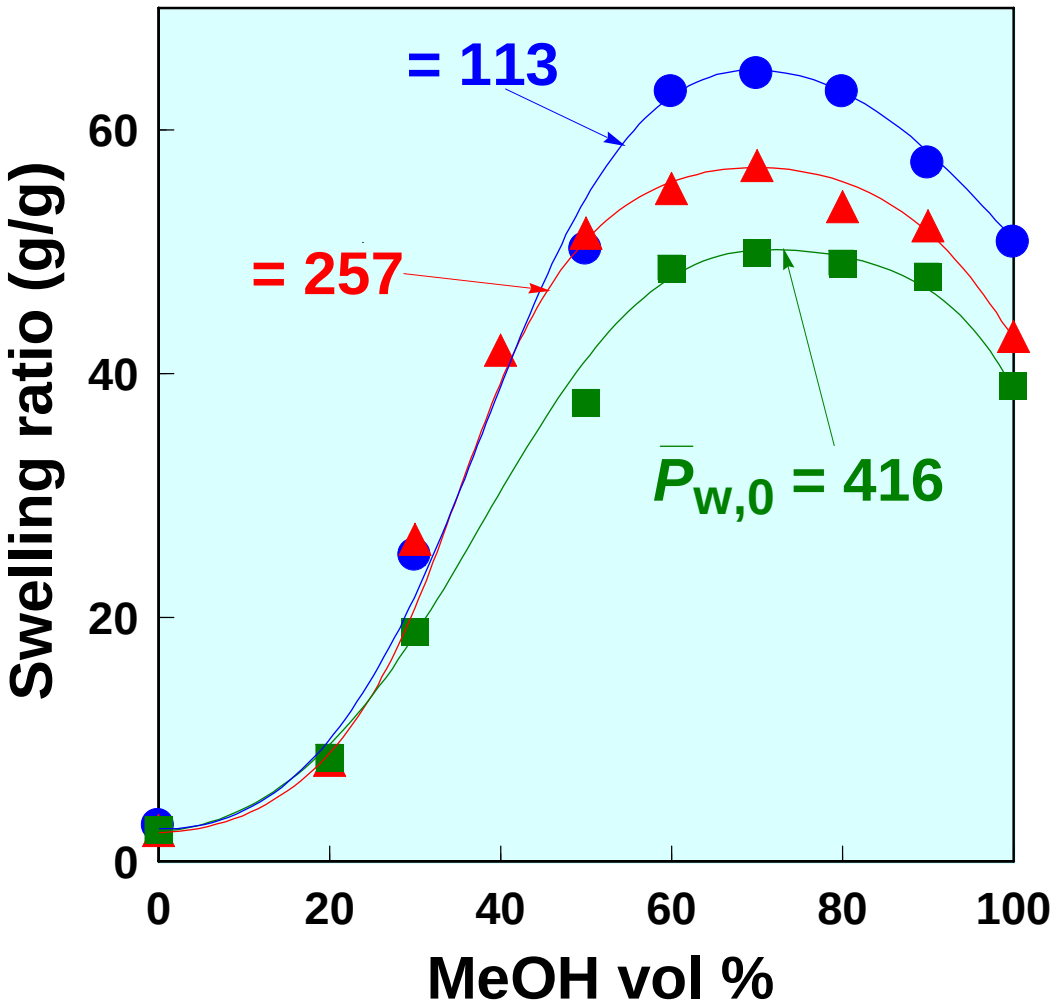


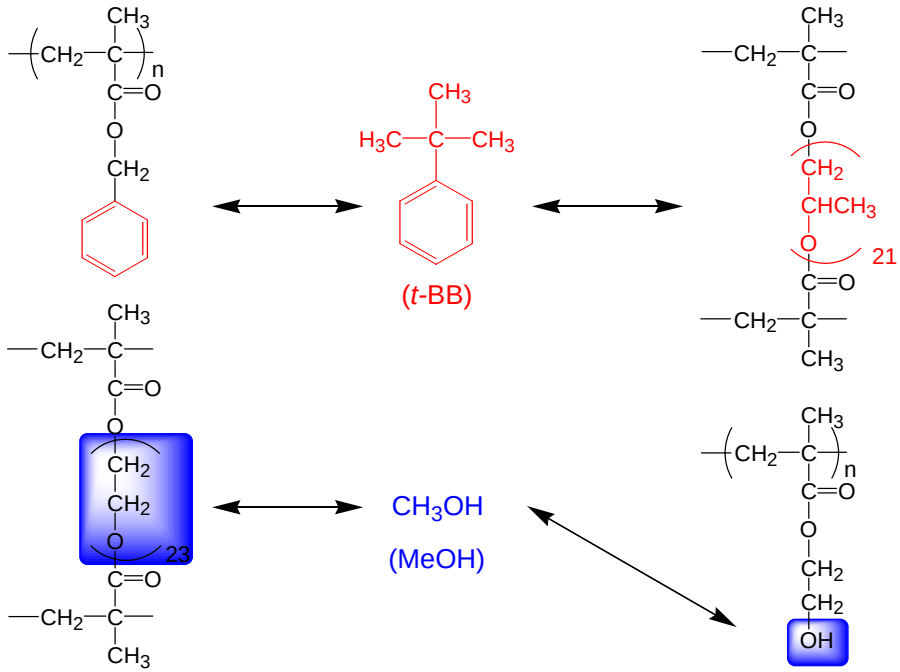
The conversion in the abscissa is corrected such that the corresponding gel point is 0% of conversion.

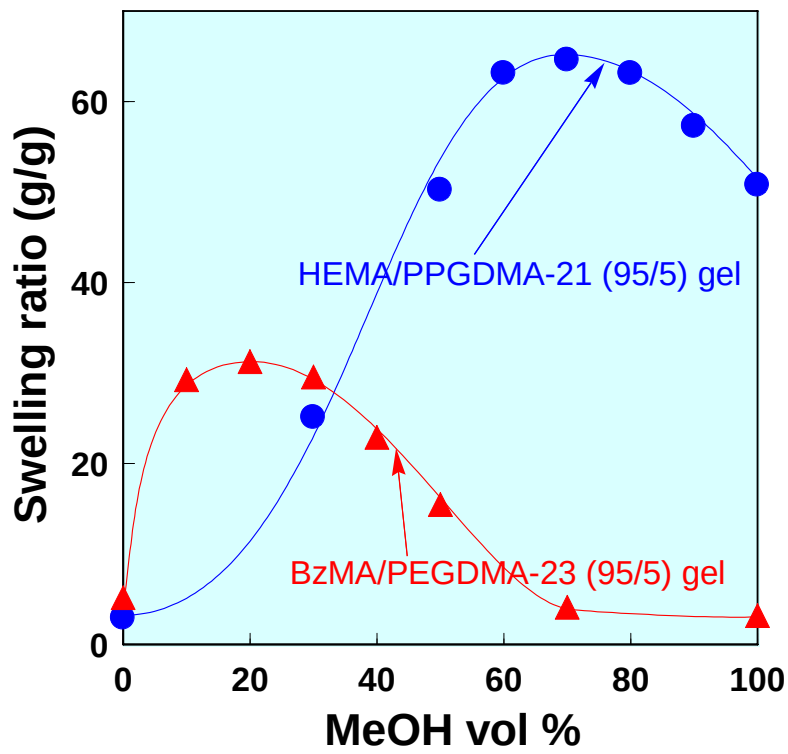
Although the swelling ratios were reduced as gelation progressed, the swelling ratios of the gels obtained just beyond the gel points were extrapolated to be quite high as a reflection of the formation of homogeneous network polymers.
Also, the swelling ratio became higher with an increase in the amount of LM as a reflection of shorter primary polymer chain length.

Correlations of swelling ratios of resulting gels with MeOH content in mixed solvents consisting of nonpolar *t*-BB and polar MeOH

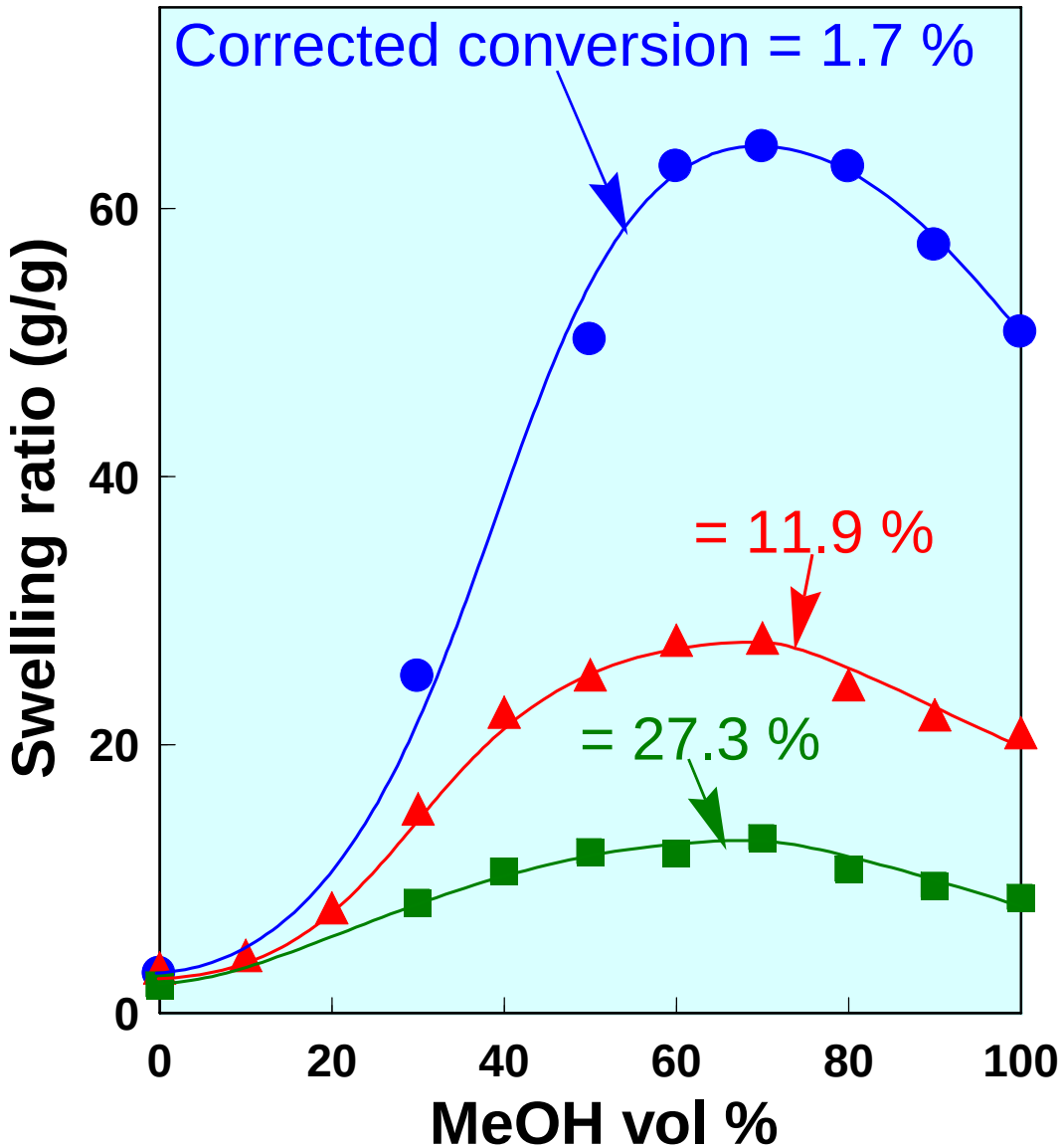
HEMA/PPGDMA-21 (95/5) copolymerizations







Conversion dependencies of characteristic swelling behavior for poly(HEMA-*co*-PPGDMA-21) gels obtained at corrected conversions



The conversion in the abscissa is corrected such that the corresponding gel point is 0% of conversion.

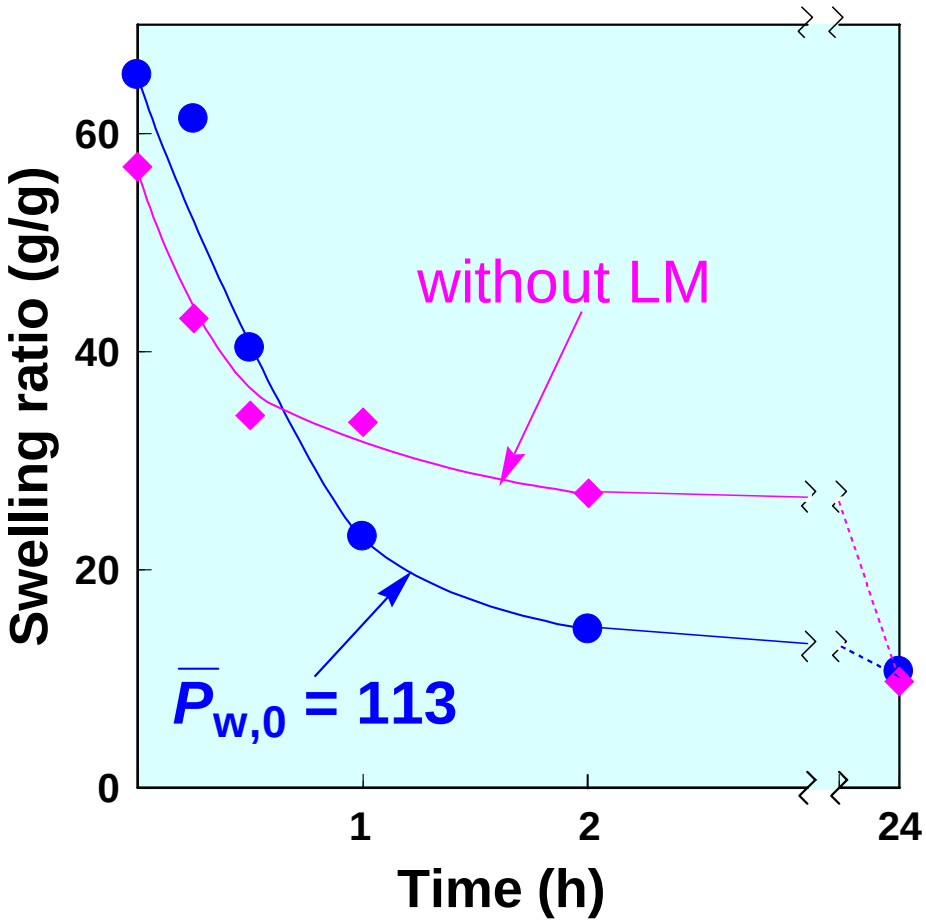
The profiles of the solvent component dependencies of the swelling ratios changed from a sharp response to a gradual one with the progress of gelation or with an increase in the crosslink density.

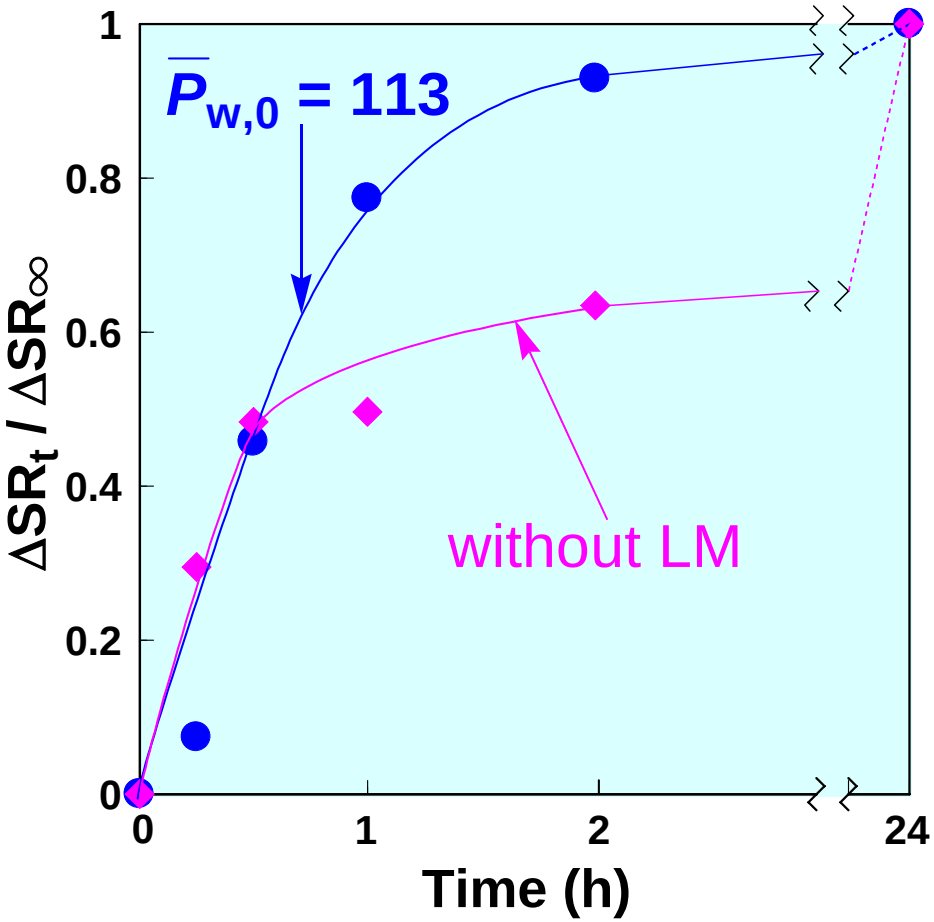
The response of the gel obtained at an early stage of gelation was sharper than that of the gel at a late stage of gelation.

Deswelling response of resulting amphiphilic lipogels

HEMA/PPGDMA-21 (95/5) copolymerizations

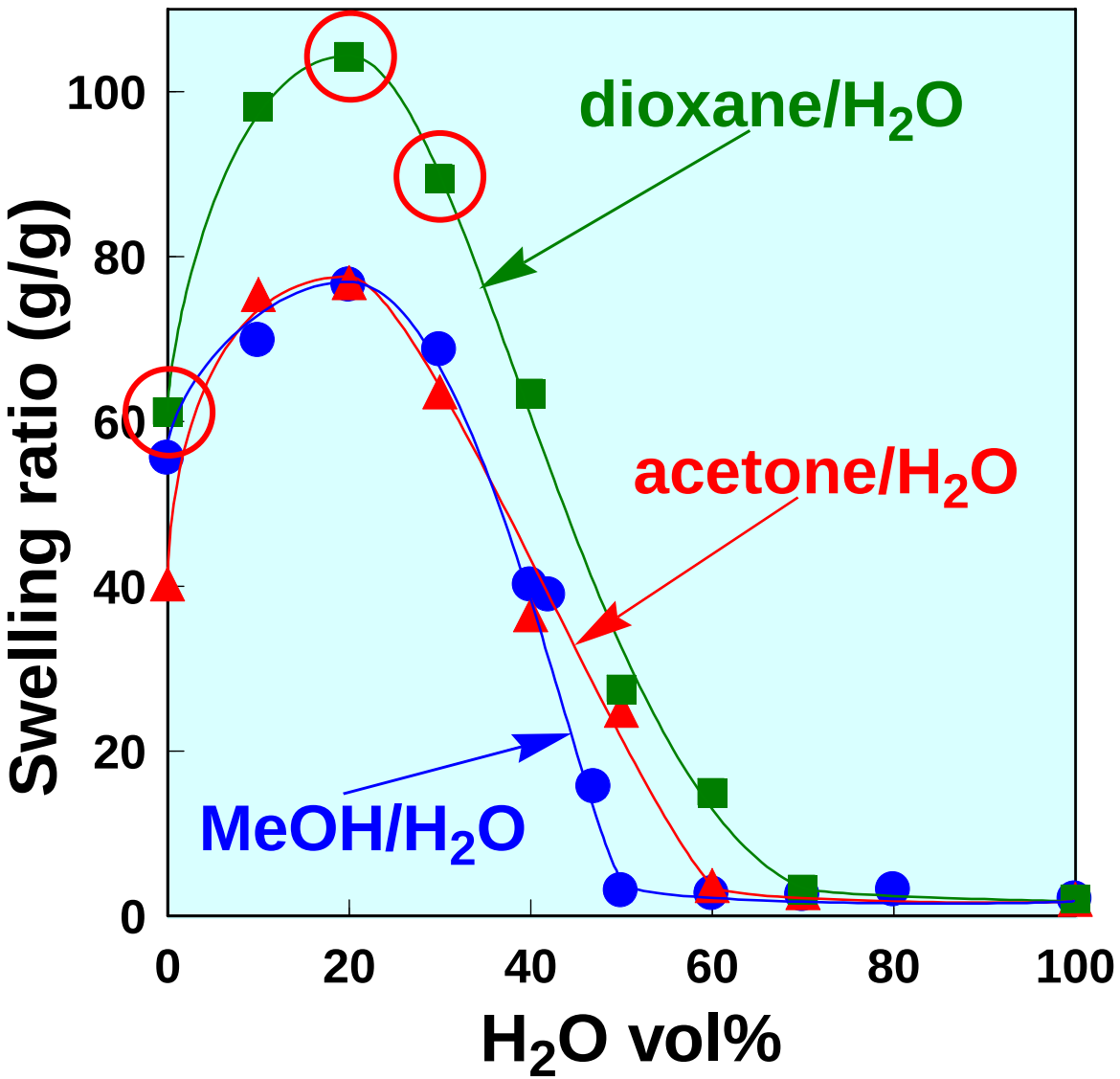
t-BB/MeOH (30/70) ⇒ *t*-BB/MeOH (80/20)





Deswelling rate of resulting amphiphilic lipogels was checked by changing the solvent polarity. The dangling chains would have a significant influence on the deswelling rate of resulting amphiphilic lipogels because of their active segmental motions.

Correlations of swelling ratios of resulting poly(HEMA-*co*-PPGDMA-21) gels with H_2O content in mixed solvents such as MeOH/H_2O, acetone/H_2O, and dioxane/H_2O mixtures

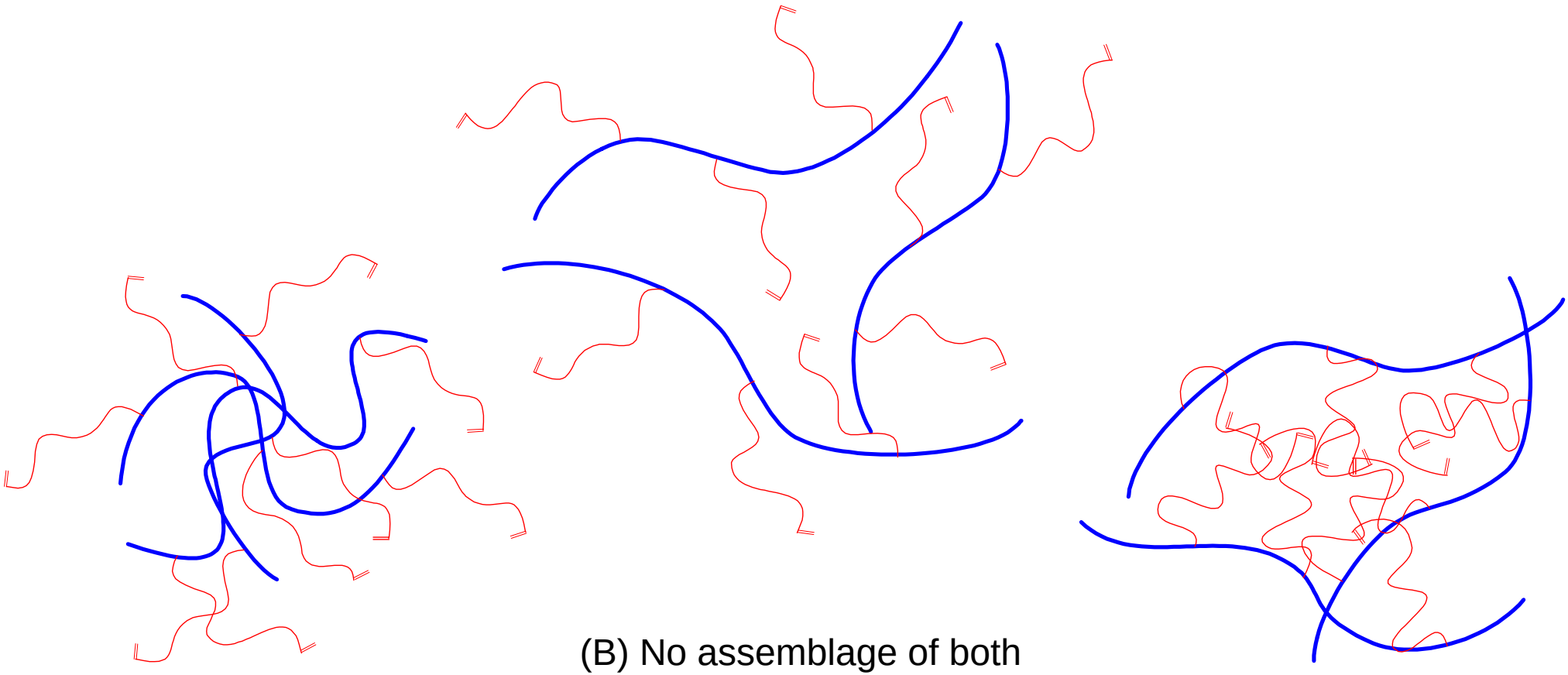


The gels obviously swelled to the largest swelling ratio up to at 20 vol % and then shrank sharply toward 50—60 vol % of H_2O.

The former may be ascribed to the collapse of intermolecular hydrogen bond between primary poly(HEMA) chains, forming a weak agglomerate, by the addition of H_2O.

The latter decreasing profile of swelling ratio with an increase in H_2O became sharper in the MeOH/H_2O solvent mixtures as a reflection of cooperative nonsolvency of both MeOH and H_2O to poly(oxypropylene) crosslink units.

Three typical conformations of amphiphilic prepolymers consisting of **short** primary polymer chains and **long** crosslink units with opposite polarities at an early stage of polymerization, where the intermolecular crosslinking would be negligible.

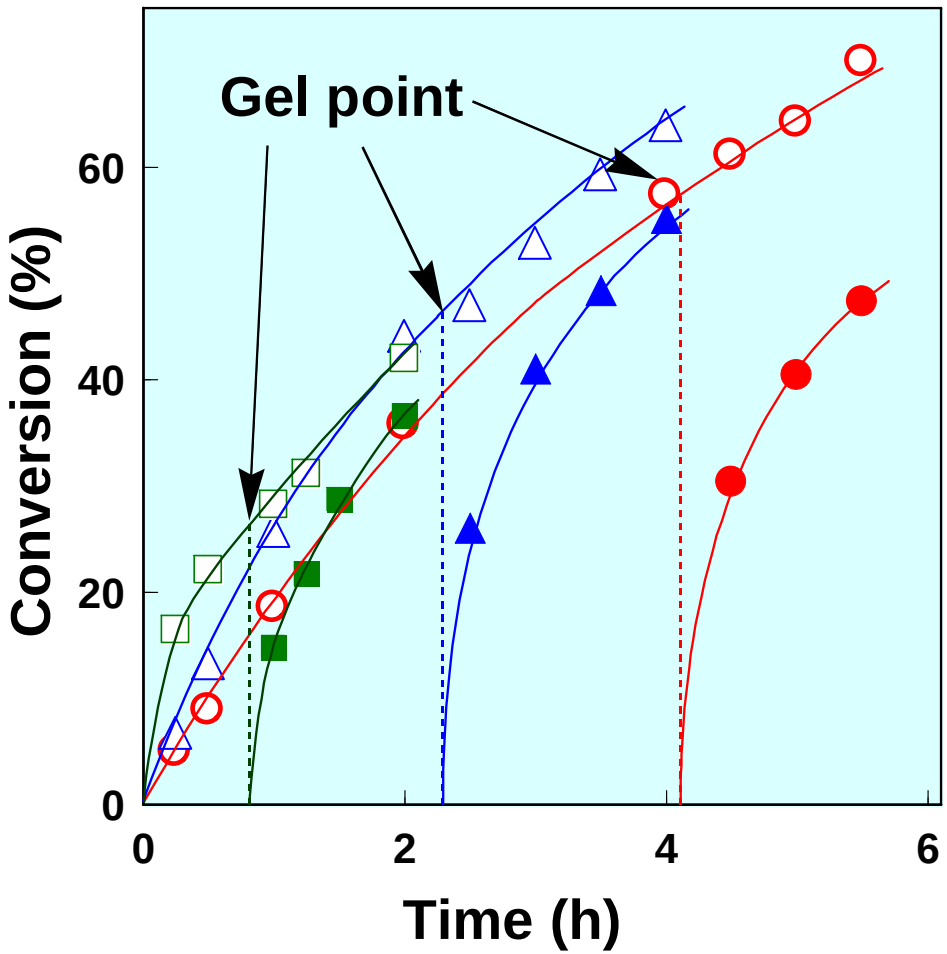


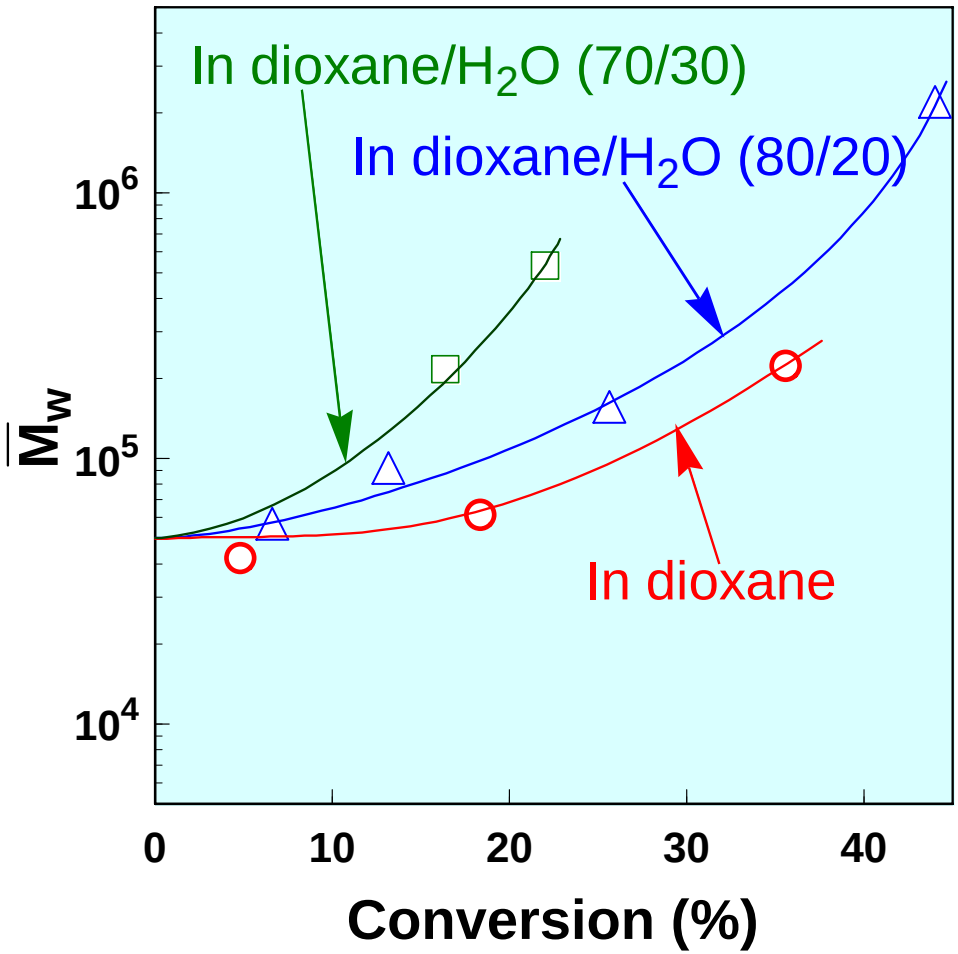
(A) Assemblage of short primary polymer chains

(B) No assemblage of both primary polymer chains and crosslink units

(C) Assemblage of long crosslink units

Solvent effect on HEMA/PPGDMA-21 (95/5) copolymerizations

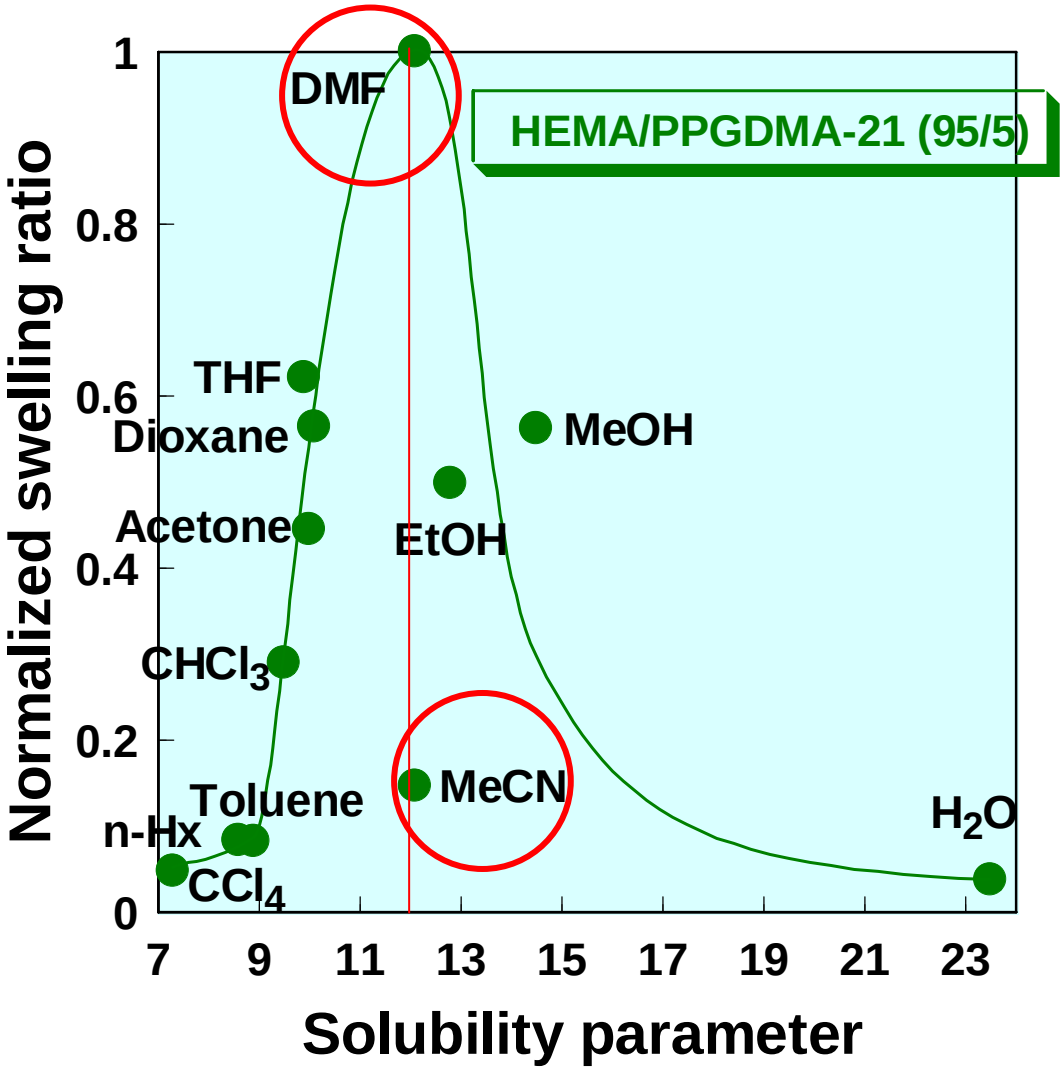


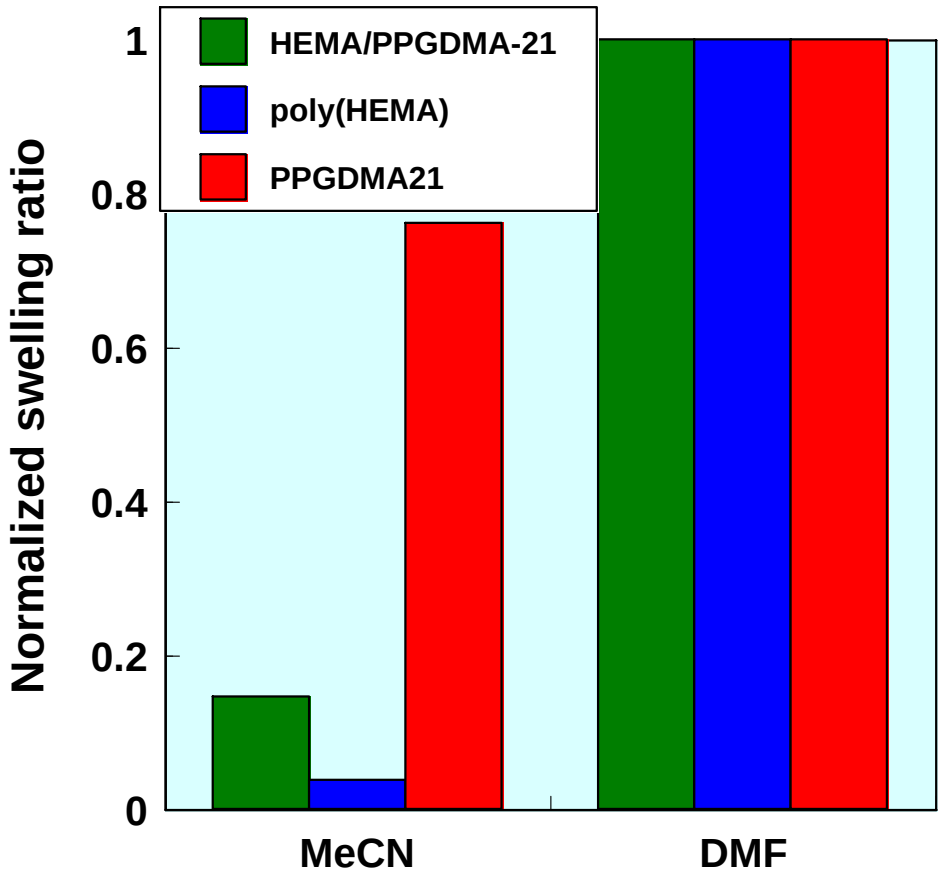


In (E,J) dioxane, (C,H) dioxane/H_2O (80/20), and (G,B) dioxane/H_2O (70/30), dilution 1/3, [AIBN] = 0.04 mol/L, 50 ℃, [LM]/[Total monomer] = 1/50.

Assemblage of short primary polymer chains caused the restricted motion of propagating polymer radical, leading to the suppression of the increment of molecular weight with conversion.
Assemblage of long crosslink units led to the promoted occurrence of intermolecular crosslinking reaction.

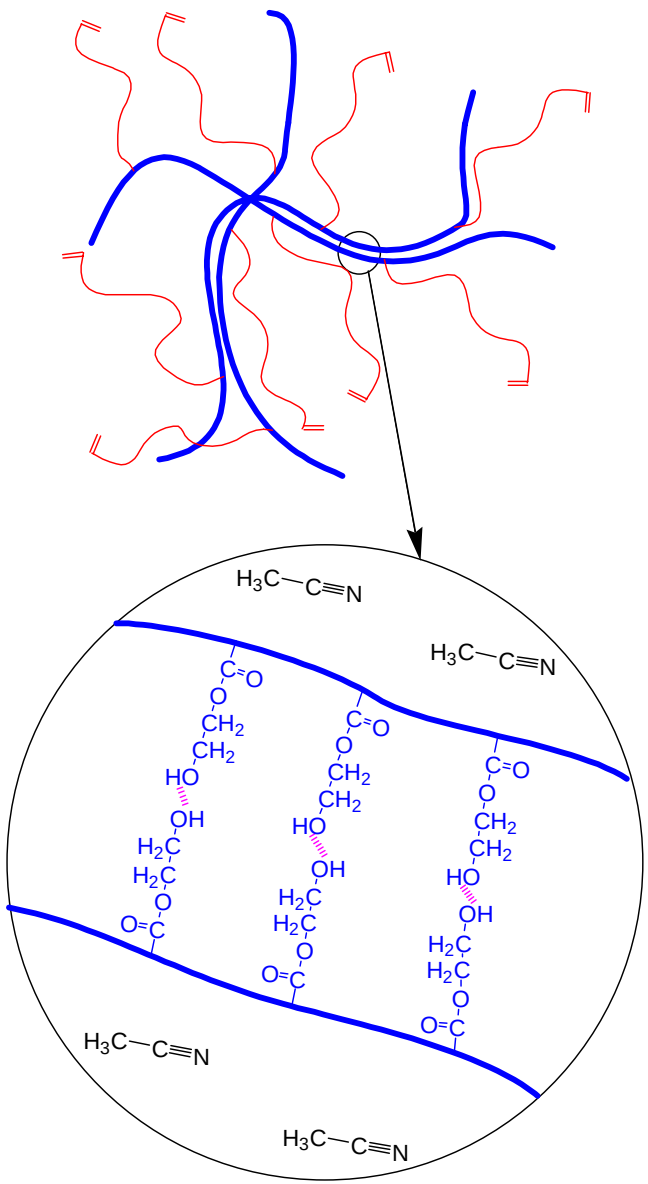
Swelling ratios of poly(HEMA-*co*-PPGDMA-21) gels in various solvents



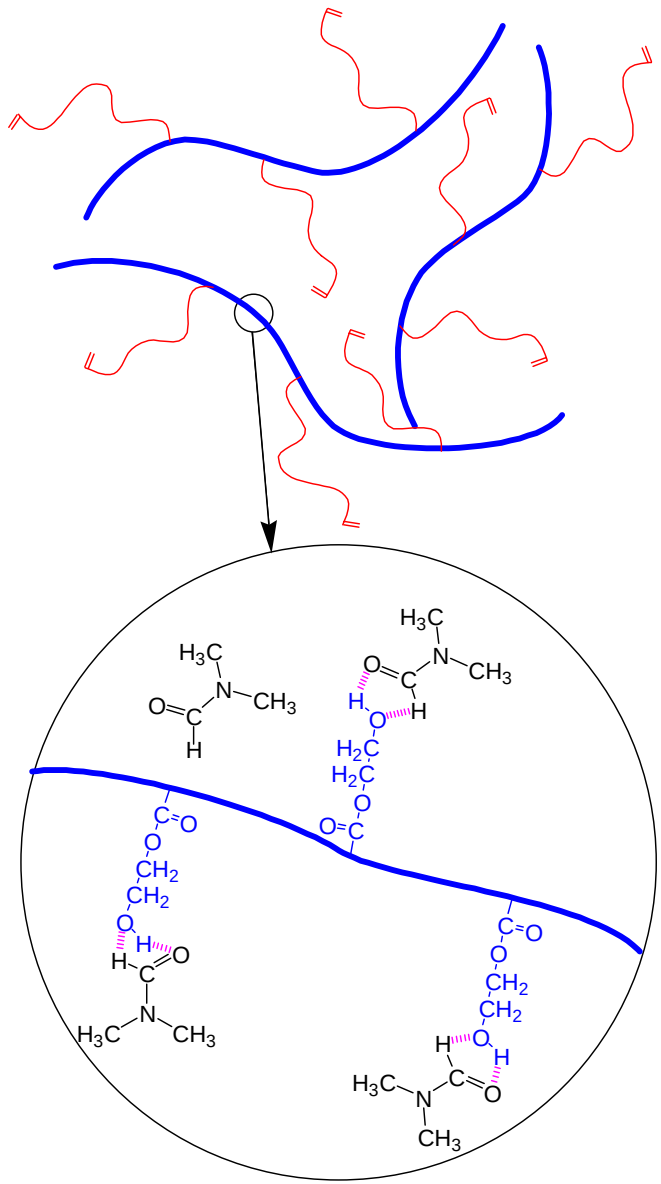


In MeCN solution, the hydrogen bonds between poly(HEMA) hydroxyl groups are stronger than the interactions between poly(HEMA) and solvent molecules.
The situation in DMF solution is vice versa.

Schematic picture of amphiphilic poly(HEMA-*co*-PPGDMA-21) prepolymers in MeCN and DMF solutions

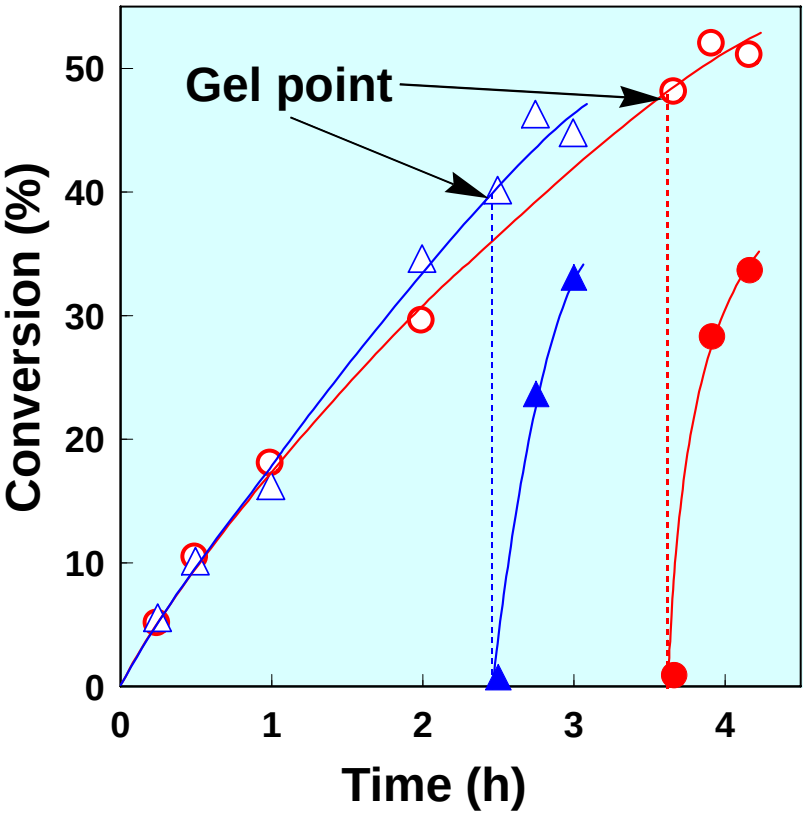


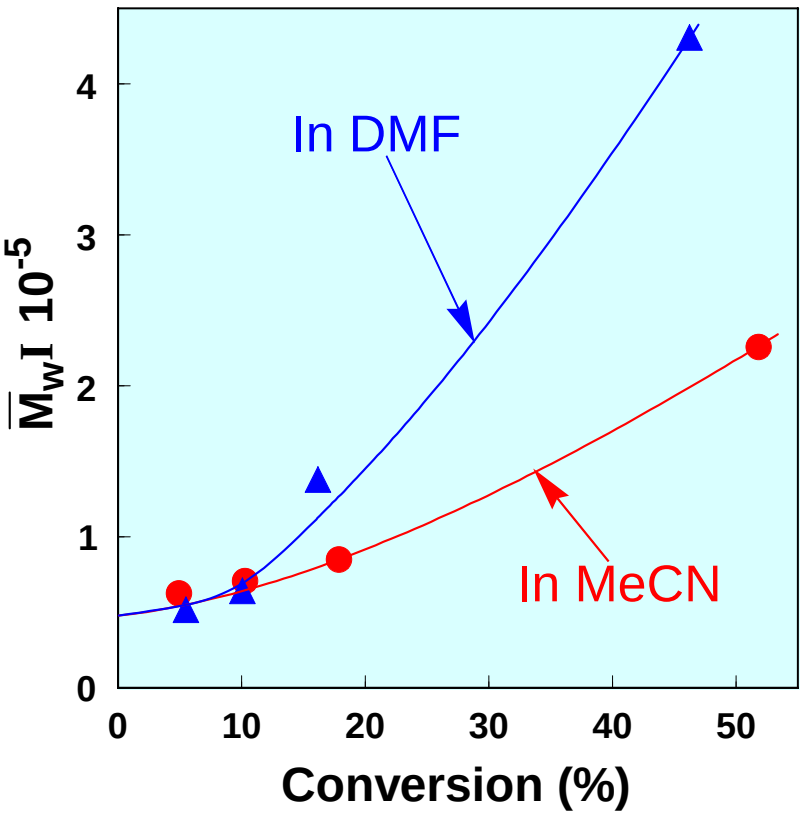
In MeCN



In DMF

Influence of physical interaction on crosslinking reaction





In MeCN In DMF

In (E,J) MeCN and (C,H) DMF,
dilution 1/3, [AIBN] = 0.04 mol/L, 50 ℃, [LM]/[Total monomer] = 1/50.

In DMF solution, both primary polymer chains and crosslink units of amphiphilic prepolymers would behave freely.

In MeCN solution, primary polymer chains having hydroxyl groups would assemble by the intermolecular hydrogen bonds between primary poly(HEMA) chains and the assemblage of primary polymer chains caused the restricted motion of propagating polymer radical leading to the suppressed occurrence of the increment of molecular weight with conversion.

Summary and Future Work

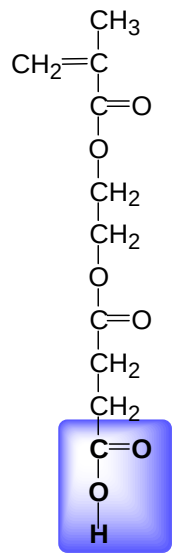
1. When the primary polymer chain length is short, the vinyl-type network polymers have abundant dangling chains. These dangling chains inherent in vinyl-type network polymers would influence as an increase in their swelling ratios and, moreover, the characteristic swelling behavior of the resulting gels.

2. The profiles of the solvent component dependencies of the swelling ratios were characteristic of novel amphiphilic gels; they became somewhat sharp with shorter primary polymer chain length as a reflection of the significance of an increased number of dangling chains.

3. The dangling chains would have a significant influence on the deswelling rate of resulting amphiphilic lipogels because of their active segmental motions.

4. The network formation might be controlled by the assemblage of both short primary polymer chains and long crosslink units. The conformation of amphiphilic prepolymers gave a great influence on their network formation.

5. We are planning to examine the influence of physical interaction on the crosslinking reaction by using MMOES having a carboxyl group with the aim to control the network formation.



Mono(2-methacryloyloxyethyl) succinate

MMOES