Preparation of Unsaturated Polyester–Silica Nanocomposites

Chan-Moon Chung,[1] Sung-Youl Cho,[1] Joong-Gon Kim,[2] Se Young Oh[3]

[1]Department of Chemistry, Yonsei University, Wonju, Kangwon-do 220-710, Korea
[2]Biotechnology Division, Hanwha Chemical R & D Center, 6 Shinsung-dong, Yusung-ku, Taejon 305-345, Korea
[3]Department of Chemical & Biomolecular Engineering, Sogang University, Seoul 121-742, Korea

ABSTRACT: Two unsaturated polyesters (UPs), PME and PMPE, were synthesized by condensation polymerization, and another UP, BPMPE, was prepared from PMPE by blocking of its carboxyl and hydroxyl end groups. Optically transparent UP–silica nanocomposites were prepared by a sol–gel process of alkoxysilanes in the presence of the UPs. Compared to the unblocked UPs, PME and PMPE, the blocked UP, BPMPE, afforded transparent nanocomposites in a wider range of feed ratio of UP/alkoxysilane. Intermolecular hydrogen bonding and π–π interaction between the organic and inorganic components were dominant factors in the nanocomposite formation when acetone was used as a solvent. Various solvents were tested and it was thought that hydrogen bonding acceptor property and boiling point of the solvents were important factors in the formation of the transparent nanocomposites. Photo-crosslinking of an UP in its nanocomposite resulted in the formation of an interpenetrating polymer network structure. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2442–2447, 2007

Key words: unsaturated polyester; nanocomposite; sol–gel; intermolecular interaction; solvent

INTRODUCTION

Unsaturated polyesters (UPs) have carbon–carbon double bonds in the main chain capable of radical crosslinking, thereby thermal or photochemical curing of an UP results in the formation of a three-dimensional network.[1–4] UPs have been widely used as thermosetting resins in industry due to their good performance properties, low cost, and ease of handling.[1,2]

Various approaches have been used to improve the performance of UP materials. One of the traditional methods is the combination of an UP with inorganic powders or fibers with micrometer dimensions.[5] We thought that if the dimension of dispersed phase in an UP composite decreases to nanometer scale or lower, the resultant nanocomposite would have some enhanced properties such as optical transparency that cannot be obtained with traditional UP composites.[6] It is expected that optically transparent UP nanocomposites could find new applications as optical materials such as lens, display, film, and coating.

One of the efficient approaches to prepare organic–inorganic nanocomposites is sol–gel process of an alkoxysilane precursor in the presence of a preformed organic polymer.[6–8] During the sol–gel reaction, the polymer molecules would be entrapped within silica network being formed, without appreciable phase separation. The nanoscale hybridization of the organic and inorganic compounds could afford transparent, homogeneous nanocomposite materials.[9]

In this study, optically transparent UP–silica nanocomposites have been prepared by sol–gel process. Intermolecular interactions between UP molecules and silica network were investigated, and solvent effect on the nanocomposite formation was also studied. For the nanocomposites obtained, photo-crosslinking of UP was carried out to obtain an interpenetrating polymer network (IPN).

EXPERIMENTAL

Materials and instruments

Maleic anhydride (MA), phthalic anhydride (PA), ethylene glycol (EG), acetic anhydride, iodomethane, pyridine, 4-methoxyphenol, benzoin methyl ether, acetone, ethanol, and N,N-dimethylformamide (DMF) were purchased from Aldrich Chemical. Iodomethane, pyridine, acetone, ethanol, and DMF were purified by distillation before use. ^{1}H NMR spectra of the UPs were taken on a Varian Gemini 300-MHz spectrometer in methyl sulfoxide (DMSO)-d_6 using tetramethylsilane as an internal standard. IR spectra were recorded on a Genisis Fourier transform infrared (FTIR) spectrophotometer (Mattson Instrument). Molecular weights of the polymers were determined

by gel permeation chromatography (GPC) using a Waters 590 equipped with a μ-styragels column. Exposure of the nanocomposite samples was made on an exposure system of Spectra Energy equipped with a 500-W high-pressure mercury lamp (light intensity: 72 mW/cm^2).

Synthesis of PME and PMPE[10]

MA (3.48 g, 0.035 mol) and EG (2.20 g, 0.035 mol) were mixed, and condensation polymerization was carried out at 195°C for 20 h, and then at 215°C for 2.5 h. Drying the product under reduced pressure gave PME as a viscous liquid.

IR (neat): 3500–2800 (carboxyl OH), 1725 (C=O), 1643 (C=C), 1164 (ester C—O). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.57–3.67 [m, end group OCH_2CH_2OH], 4.06–4.18 [m, end group OCH_2CH_2OH], 4.38–4.43 [m, main chain OCH_2CH_2O], 6.27–6.78 [m, CH=CH].

Another polyester PMPE was prepared in a similar manner using a molar ratio of MA:PA:EG of 1 : 1 : 2. MA (3.48 g, 0.035 mol), PA (5.24 g, 0.035 mol), and EG (4.40 g, 0.070 mol) were mixed, and condensation polymerization was carried out at 195°C for 20 h, and then at 215°C for 2.5 h. Drying the product under reduced pressure gave PMPE as a viscous liquid.

IR (neat): 3500–2800 (carboxyl OH), 1728 (C=O), 1646 (C=C), 1276 (ester C—O). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 3.62–3.67 [m, end group OCH_2CH_2OH], 4.14–4.24 [m, end group OCH_2CH_2OH], 4.43–4.54 [m, main chain OCH_2CH_2O], 6.65–6.78 [m, CH=CH], 7.60–7.80 [br. s, aromatic].

End group-blocking of PMPE

First, the hydroxyl end groups of PMPE were blocked by acetylation using acetic anhydride. To a solution of PMPE (30 g) in acetone (100 mL) were added acetic anhydride (56.6 mL, 0.60 mol) and pyridine (48.5 mL, 0.60 mol), and the resultant solution was stirred for 12 h at room temperature. Dichloromethane was added to the reaction mixture, followed by washing with water three times. Removal of the solvent under reduced pressure gave a PMPE having acetoxy end groups. In the second step, the remaining carboxyl end groups of PMPE were blocked by esterification using iodomethane. The partially blocked PMPE (25 g) was dissolved in acetone (100 mL), and K$_2$CO$_3$ was added to the resulting solution, which was stirred for 3 h. After adding CH$_3$I (16.8 mL, 0.27 mol) the mixture was stirred for 4 h at 56°C. After removal of a part of acetone, dichloromethane was added and the resultant solution was washed with water and an aqueous KOH. The solvent (dichloromethane) was removed to obtain BPMPE. The overall yield of end-blocking of PMPE was 72%.

IR (neat): 1728 (C=O), 1646 (C=C), 1276 (ester C—O). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.01 [s, OCOCH_3], 3.72–3.82 [m, COOCH_3], 4.33–4.48 [m, OCH_2CH_2O], 6.71 [s, CH=CH], 7.60–7.80 [br. s, aromatic].

Preparation of UP–silica nanocomposites

An alkoxysilane was added to an acetone solution of an UP, benzoin methyl ether (3 mol % with respect to C=C bond of the UP), and 4-methoxyphenol (0.25 mol % with respect to C=C bond of the UP). An aqueous HCl (equivalent to methoxy groups of alkoxysilane) was then added as catalyst to the resulting solution. The benzoin methyl ether, a typical photoinitiator in free radical photocure systems,[11] was employed to initiate photo-crosslinking. The mixture was heated at 60°C for 1 week to allow sol–gel reaction. Similar synthesis was also conducted by using ethanol or DMF instead of acetone for the investigation of solvent effect.

Measurement of photo-crosslinking conversion of nanocomposites

KBr pellets containing the nanocomposite powders were prepared and exposed to UV light to initiate crosslinking of UP. The measurement of crosslinking conversion was carried out with the FTIR spectrophotometer. The ratios of calculated areas of the two absorption bands (1646 cm^{-1} for C=C and 1728 cm^{-1} for C=O) before and after exposure were compared to determine the degree of conversion of the C=C bonds.[12] The absorption band at 1728 cm^{-1} was used as an internal standard for the conversion determination.

Investigation of solvent-resistant property of nanocomposites

A nanocomposite sample of 100 mg was ground in a mortar and photoirradiated for 4 h. Each sample was then extracted with 250 mL of chloroform in a Soxhlet extractor for 24 h. The solvent was removed under reduced pressure to measure the mass of the extracted species. The mass value was converted to a fraction (%) of the initial sample mass.

RESULTS AND DISCUSSION

Two UPs, PME and PMPE, have been prepared by condensation polymerization, and their structures are shown in Figure 1. End-group-blocking of PMPE was carried out to obtain BPMPE by acetylation of hydroxyl groups with acetic anhydride, followed by esterification of carboxyl groups with methyl iodide (Scheme 1). The chemical structures of PME, PMPE,
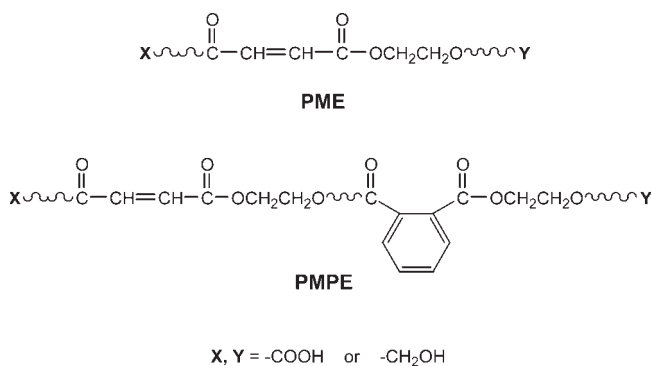
Figure 1 Structures of PME and PMPE.

and BPMPE were characterized by ^{1}H NMR and FTIR spectroscopy. The number and weight average molecular weights of the three UPs were measured by GPC and summarized in Table I. Polydispersity index of the three UPs ranged from 2.0 to 3.7.

Three alkoxysilanes were employed as a precursor of silica (Fig. 2). The UPs and alkoxysilanes well dissolved in acetone, ethanol, and DMF. The sol–gel reactions of the alkoxysilanes were carried out at 60°C using HCl catalyst in the presence of the UPs. It was confirmed by NMR spectroscopy that the UPs were intact under the reaction conditions. Hard composite monoliths were obtained after the sol–gel process. FTIR spectra of the composites showed a characteristic absorption of Si—O—Si at 1035 cm^{-1}, indicating the formation of silica network.

In order for a composite to be optically transparent, the domain size of dispersed phase must be smaller than ⁓200 nm.[13,14] In this study, optical transparency

was used as a criterion for the formation of a homogeneous nanocomposite composed of UP and silica.

The preparation of UP–silica nanocomposite was attempted by using acetone as a solvent (Table II). Transparent nanocomposite could not be obtained from the combination of PME and any of the three alkoxysilanes (runs 1–9). It was considered that PME has a strong self-association tendency because of carboxyl and hydroxyl end groups capable of self-hydrogen bonding,[15,16] leading to the phase separation during the sol–gel process. In the case of PMPE, nanocomposite formation was not observed when TMOS or MeTMOS was combined (runs 10–15). Formulations based on PMPE–PhTMOS also gave turbid composites at their mass ratios of 1/2, 1/1, and 2/1 (runs 19–21). Transparent PMPE–silica nanocomposites were only obtained at lower ratios of PMPE/PhTMOS of 1/20, 1/10, and 1/4 (runs 16–18). These results indicate that PMPE has a self-association tendency as in the case of PME, so precipitated during the sol–gel process at higher concentrations of PMPE. Actually the IR spectra of the sol–gel products derived from PME and PMPE did not show any carboxyl (or hydroxyl) absorption that is free from hydrogen bonding: characteristic absorption due to free carboxyl or hydroxyl groups was not observed above 3500 cm^{-1}.[17]

Two kinds of intermolecular interactions would be responsible for the formation of transparent nanocomposites from PMPE/PhTMOS (runs 16–18): hydrogen bonding between carbonyl groups in PMPE and unreacted silanol groups in the silica network, and π–π interactions between benzene rings in PMPE
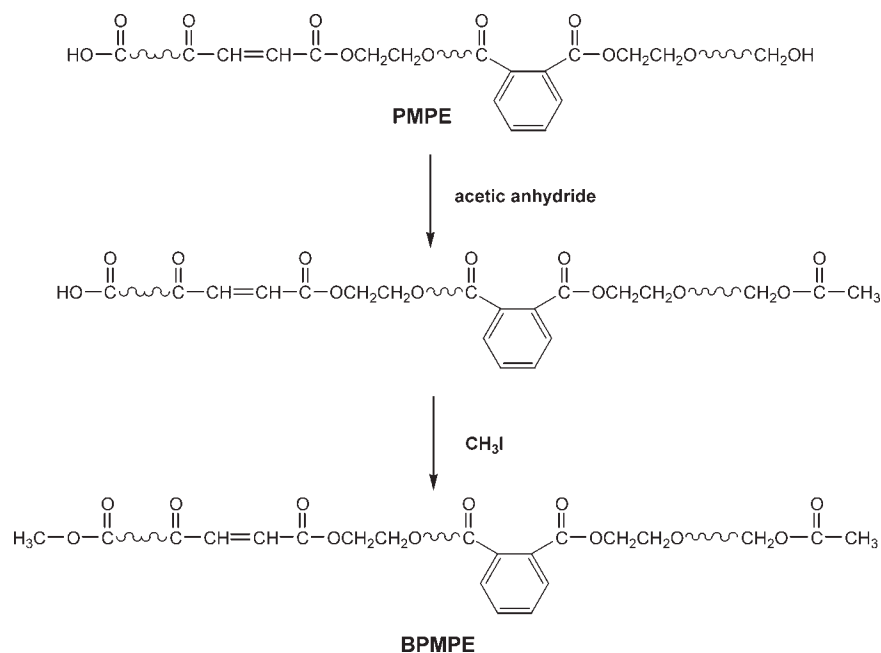
Scheme 1

TABLE I
Molecular weight of UPs

UP	Molecular weight (g/mol)	
	Number average	Weight average
PME	960	2270
PMPE	1360	5000
BPMPE	1570	4510

and those in the silica. At lower concentrations of PMPE (runs 16–18), these interactions might be important for the homogeneous dispersion of PMPE molecules in the silica network. However, as the content of PMPE increases (runs 19–21), the self-association of PMPE molecules due to the self-hydrogen bonding would become dominant, leading to phase separation. Covalent bond formation by the reaction of carboxyl (or hydroxyl) end groups in PMPE with silanol groups in silica gel is not likely to occur because the resulting bonds are very unstable under the usual sol–gel reaction conditions.[18]

In order to decrease the self-association tendency of PMPE, its carboxyl and hydroxyl end groups were blocked. The modified PMPE (BPMPE) was used as an organic polymer in the sol–gel process. When BPMPE was combined with PhTMOS, transparent nanocomposites were obtained in a wide range of composition of 1/20 to 4/1 (runs 22–28). The elimination of self-hydrogen bonding of PMPE, as expected, resulted in effective interactions between BPMPE and silica network being formed, leading to the formation of nanocomposites in a wider range of UP/silica composition. The resultant homogeneity would be attributable to hydrogen bonding between carbonyl groups in BPMPE and silanol groups in silica network, and π–π interactions between benzene rings in BPMPE and those in PhTMOS-derived silica.

It is interesting that turbid composites were obtained from the combination of BPMPE and TMOS without π–π interaction (runs 29–31). This suggests that the π–π interaction played an important role in the nanocomposite formation from BPMPE/PhTMOS. Thus far, π–π interaction has been only utilized in a few cases of nanocomposite synthesis, for example, in order to prepare polystyrene–silica gel nanocomposites.[19] Although it was difficult to obtain spectroscopic evidence for π–π interaction and hydrogen bonding between UPs and silica in this study, we
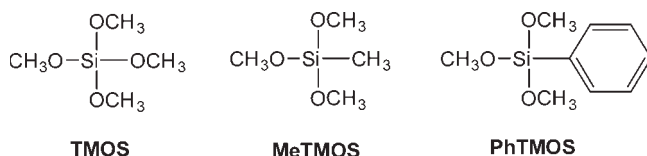

Figure 2 Structures of alkoxysilanes.

TABLE II
Preparation of UP-silica nanocomposites[a]

Run	UP	Alkoxysilane	Ratio[b]	Appearance
1	PME	TMOS	1/20	Turbid
2	PME	TMOS	1/4	Turbid
3	PME	TMOS	1/1	Turbid
4	PME	MeTMOS	1/20	Turbid
5	PME	MeTMOS	1/4	Turbid
6	PME	MeTMOS	1/1	Turbid
7	PME	PhTMOS	1/20	Turbid
8	PME	PhTMOS	1/4	Turbid
9	PME	PhTMOS	1/1	Turbid
10	PMPE	TMOS	1/20	Turbid
11	PMPE	TMOS	1/4	Turbid
12	PMPE	TMOS	1/1	Turbid
13	PMPE	MeTMOS	1/20	Turbid
14	PMPE	MeTMOS	1/4	Turbid
15	PMPE	MeTMOS	1/1	Turbid
16	PMPE	PhTMOS	1/20	Transparent
17	PMPE	PhTMOS	1/10	Transparent
18	PMPE	PhTMOS	1/4	Transparent
19	PMPE	PhTMOS	1/2	Turbid
20	PMPE	PhTMOS	1/1	Turbid
21	PMPE	PhTMOS	2/1	Turbid
22	BPMPE	PhTMOS	1/20	Transparent
23	BPMPE	PhTMOS	1/10	Transparent
24	BPMPE	PhTMOS	1/4	Transparent
25	BPMPE	PhTMOS	1/2	Transparent
26	BPMPE	PhTMOS	1/1	Transparent
27	BPMPE	PhTMOS	2/1	Transparent
28	BPMPE	PhTMOS	4/1	Transparent
29	BPMPE	TMOS	1/20	Turbid
30	BPMPE	TMOS	1/4	Turbid
31	BPMPE	TMOS	1/1	Turbid

[a] Alkoxysilane 0.50 g, acetone 5 mL, aqueous HCl 2M, water eq to methoxy groups of alkoxysilane.
[b] Feed ratio of UP to alkoxysilane (w/w).

could make some reasonable presumptions about the intermolecular interactions as described earlier, based on the results of the sol–gel synthesis.

Solvent effect was investigated by using acetone, ethanol, and DMF in the preparation of UP/TMOS-based nanocomposite (Table III). It should be noted that TMOS-derived silica gel do not form π–π interaction due to the lack of aromatic group. Ethanol and DMF were selected since they are known to act as stronger hydrogen bonding acceptors than acetone.[20] The normal boiling points of pure acetone, ethanol, and DMF are 56, 78, and 153°C, respectively. Opaque composites were generated from PMPE/TMOS when acetone or ethanol was used. In the experiments with DMF, however, transparent nanocomposites were obtained in a wide range of composition of PMPE/TMOS (Table III). This might be attributable to the following two factors. First, DMF is a relatively good hydrogen bonding acceptor, thus could prevent the self-association of PMPE molecules: DMF can form hydrogen bonding with carboxyl and hydroxyl end groups in PMPE. Second, DMF has a higher boiling point than acetone and ethanol have: PMPE

TABLE III
Formation of transparent UP/TMOS-derived nanocomposites[a]

Solvent	UP	
	PMPE[b]	BPMPE[b]
Acetone	None	None
Ethanol	None	None
Acetone/DMF (1/1 by vol.)	None	1/20, 1/10, 1/4, 1/2, 1/1
DMF	1/20, 1/10, 1/4, 1/2, 1/1, 2/1	1/20, 1/10, 1/4, 1/2, 1/1, 2/1, 3/1

[a] TMOS 0.50 g, solvent 5 mL, aqueous HCl 2M, water eq to methoxy groups of TMOS.
[b] Feed ratio of UP to TMOS (w/w) that gave transparent nanocomposites.

molecules remained homogeneously dissolved in DMF until they were entrapped in silica network being formed. It is considered that the boiling point of solvent was probably a more important factor in the nanocomposite formation than the intermolecular interactions, based on the results that the sol–gel reactions with ethanol did not give transparent nanocomposite despite its higher hydrogen bonding acceptor property than DMF.[20]

BPMPE/TMOS also did not give transparent composite when acetone or ethanol was used. It is thought that acetone and ethanol have relatively low boiling points, thus evaporated before physical entrapment of the BPMPE molecules in silica gel network occurred. In the synthesis with DMF, however, BPMPE/TMOS gave transparent nanocomposites. Even the use of a 1 : 1 mixture (by volume) of acetone and DMF resulted in transparent products. The elimi-

nation of self-hydrogen bonding of PMPE could offer a wider choice of solvent for the preparation of the transparent nanocomposites.

The nanocomposites obtained are considered to be a class of semi-IPN having linear polymer molecules entrapped in a three-dimensional silica network. The photo-crosslinking of the nanocomposite should result in the formation of an IPN structure in which both the organic and inorganic polymers have physical interlocking between them.[21] The photo-crosslinking behavior of the BPMPE–silica nanocomposite was investigated using FTIR spectroscopy. The absorption at 1646 cm^{-1} representing the C=C stretching vibration gradually decreased with increasing exposure time, indicating the photo-crosslinking of BPMPE (Fig. 3). As shown in Figure 4, the BPMPE/TMOS (1/4) nanocomposites revealed a conversion of 68% when irradiated for 45 min. The nanocomposite derived from BPMPE/TMOS showed much lower conversion than did BPMPE alone. This is probably due to that the dispersion of BPMPE molecules and the restriction of their movement in the silica matrix. After crosslinking, the BPMPE–silica nanocomposite showed enhanced solvent resistance compared to the semi-IPN nanocomposite: the percent elution reduced from 14% to 8% upon irradiation. This result sup-
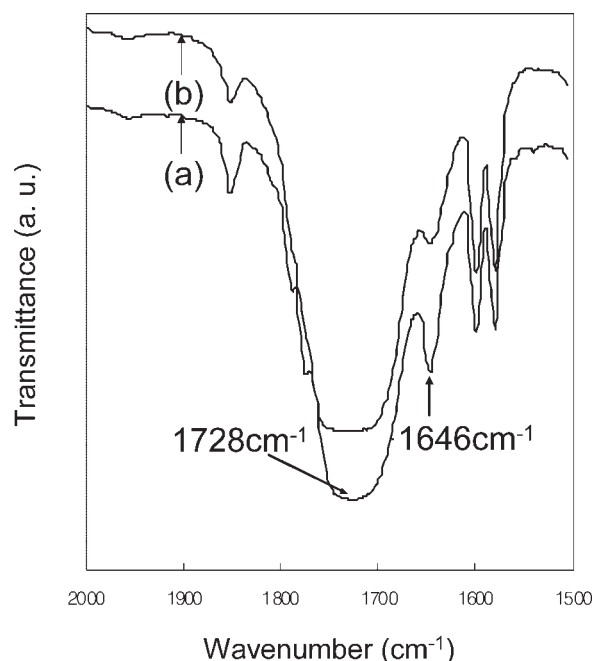

Figure 3 IR spectra of a nanocomposite derived from BPMPE/TMOS (1/4) (a) before and (b) after photoirradiation for 45 min.
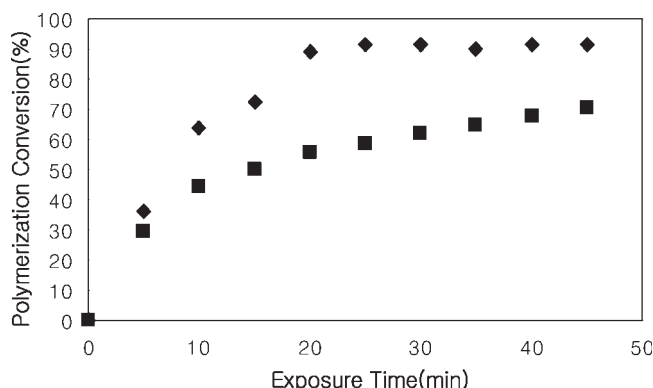

Figure 4 Plot of conversions of a BPMPE (♦) and a nanocomposite derived from BPMPE/TMOS (■) (1/4) vs. exposure time.

ported the formation of the IPN structure by photo-crosslinking.[22]

CONCLUSION

Compared to the unblocked UPs, PME and PMPE, the blocked UP, BPMPE, afforded transparent nanocomposites in a wider range of UP/silica composition. It is considered that hydrogen bonding and π–π interaction between UP molecules and silica gel were dominant factors for the nanocomposite formation. The sol–gel process with DMF solvent gave UP/TMOS-derived nanocomposites in a wide range of composition, probably because it has better hydrogen bonding acceptor property and higher boiling point than acetone has. The IPN structure of UP–silica gel was achieved by the photo-cross-linking of BPMPE in its nanocomposite.

References

1. Gunduz, G. In Polymeric Materials Encyclopedia; Salamone, J. C., Ed.; CRC Press: Boca Raton, 1996.
2. Stevens, M. P. Polymer Chemistry: An Introduction; Oxford University Press: New York, 1999.
3. Sadafule, D. S.; Panda, S. P. J Appl Polym Sci 1979, 24, 511.
4. Alexander, I. J.; Scott, R. J. Brit Polym J 1983, 15, 30.
5. Varma, I. K.; Gupta, V. B. In Comprehensive Composite Materials; Kelly, A.; Zweben, C., Eds.; Elsevier: Oxford, 2000.
6. Novak, B. M. Adv Mater 1993, 5, 422.
7. Ke, Y. C.; Stroeve, P. Polymer-layered Silicate and Silica Nanocomposites; Elsevier: Amsterdam, 2005.
8. Wen, J.; Wilkes, G. L. Chem Mater 1996, 8, 1667.
9. Chujo, Y.; Tamaki, R. MRS Bull 2001, May, 389.
10. Chung, C.-M.; Lee, S.-J.; Kim, J.-G.; Jang, D.-O. J Non-Cryst Solids, 2002, 311, 195.
11. Ledwith, A. In Photochemistry and Polymeric Systems; Kelly, J. M.; McArdle, C. B.; Maunder, M.J.F., Eds.; Royal Society of Chemistry: Cambridge, 1993; p 1.
12. Chung, C.-M.; Kim, J.-G.; Choi, J.-H. J Appl Polym Sci 2000, 77, 1802.
13. Landry, C. J. T.; Coltrain, B. K.; Wesson, J. A.; Zumbulyadis, N.; Lippert, J. L. Polymer 1992, 33, 1496.
14. Hu, Q.; Marand, E. Polymer 1999, 40, 4833.
15. Zheng, H.; Zheng, S.; Guo, Q. J Polym Sci Polym Chem 1997, 35, 3169.
16. Demmler, K.; Gunzler, G. Makromol Chem 1966, 90, 119.
17. Pretsch, E.; Buhlmann, P.; Affolter, C. Structure Determination of Organic Compounds; Springer: Berlin, 2000.
18. Kohjiya, S.; Ochiai, K.; Yamashita, S. J Non-Cryst Solids 1990, 119, 132.
19. Tamaki, R.; Samura, K.; Chujo, Y. Chem Commun 1998, 1131.
20. Kim, S. C.; Park, M. O. Hwahakhoe Chi 1988, 32, 249.
21. Sperling, L. H.; Mishra, V. Polym Adv Technol 1996, 7, 197.
22. Imai, Y.; Naka, K.; Chujo, Y. Polym J 1998, 30, 990.