Embedding Nanofibers in a Polymer Matrix by Polymerization of Organogels Comprising Heterobifunctional Organogelators and Monomeric Solvents

Suk Hoon Kang, Byung Mun Jung, Woo Jin Kim, and Ji Young Chang*

Department of Materials Science and Engineering, and Hyperstructured Organic Materials Research Center, Seoul National University, San 56-1, Shillim-dong, Gwanak-gu, Seoul 151-744, Korea

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We demonstrate the embedding of nanofibers in a polymer matrix through the polymerization of an organogel. A series of organogelators based on a biphenyl ester having two different polymerizable groups, namely, acryl and diacetylene groups, are prepared. The resulting heterobifunctional gelators show the ability to gelate various monomeric solvents. The photopolymerization of an organogel of a heterobifunctional gelator (1.5 or 10 wt %), formed in hexyl methacrylate (HMA), is carried out by UV irradiation in the presence of 2,2-dimethoxy-2-phenylacetophenone (photoinitiator, 4 wt %). The polymerization of HMA forms a polymer matrix, while the polymerization of the acryl and diacetylene groups of the gelator forms the nanofibers with a cross-linked structure. The copolymerization of a gelator and HMA at the interface will improve the adhesion between the nanofiber and the polymer matrix. The polymerized gels appear yellowish and exhibit strong fluorescence when irradiated with 365 nm UV light. This is due to the presence of polydiacetylene chains. The fluorescent polydiacetylene nanofibers embedded in the polymer matrix are visualized by using confocal laser scanning microscopy. The thermal and mechanical properties of the nanofibers embedded in polyHMA are investigated using differential scanning calorimetry, dynamic mechanical analysis, and a universal testing machine. The polymerized gels show improved thermal and physical properties in comparison to the matrix polymer (polyHMA).

Introduction

Organogels are thermoreversible and viscoelastic materials, consisting of low molecular weight gelators and organic solvents.[1–9] They have a unique structural feature in that the nanosized fibers, formed by the self-assembly of the gelator molecules, are finely distributed in a gel composed mainly of solvent molecules.[10–13] A precisely controlled and fully dispersed morphology of the fibrils is paramount for optimizing the mechanical and physicochemical properties of a material. However, these supramolecular structures are easily collapsed or changed by small perturbations in the environmental conditions, and the use of organogels in advanced materials is limited by their poor stability. The polymerization in the supramolecular state has been widely used to provide the soft supramolecular assemblies of small mass molecules with physicochemical stability. For example, the polymerization of hydrated amphiphiles yields polymeric materials having various supramolecular structures, such as lamellar and vesicular structures.[14] The polymerization of reactive mesogens in an oriented liquid crystalline state produces anisotropic polymeric films.[15–21]

The polymerization of organogels can be carried out in two different ways: by using a polymerizable gelator[22–30]

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* Corresponding author. Fax: (+82)2-885-1748. E-mail: jichang@snu.ac.kr.

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or by using a monomeric solvent.[31,32] Several research groups reported photopolymerizable organogelators containing a methacrylate[22,23] or a diacetylene group.[24–30] The groups of Möller and Weiss have studied the polymerization of an organogel formed in a monomeric solvent. Möller and coworkers[31] prepared a 3,4,5-tris(octyloxy)benzamide organogelator, which gelated a monomeric solvent. They were able to maintain a gel structure permanently by low-temperature curing in the presence of a cross-linker. Weiss and coworkers[32] showed that a mesoscopic channel with a submicrometer diameter could be generated by the removal of a gelator molecule (tetraoctadecylammonium bromide) from a polymerized gel in methylmethacrylate or styrene.

We previously demonstrated the first example of a heterobifunctional organogelator having two different photopolymerizable groups, namely, an acryl group and a diacetylene group.[33] In this work, we prepared a series of heterobifunctional organogelators and investigated their gelation and polymerization behaviors. We were particularly interested in the organogels formed in a monomeric solvent. It was expected that the in situ polymerization of an organogel comprising a polymerizable gelator and a monomeric solvent would form polymeric nanofibers that are embedded and distributed evenly in a polymer matrix. The uniform distribution of nanofibers is always of great concern in the fabrication of a polymer nanocomposite. Here we report the morphology and the physical properties of the polymerized gels.

Experimental Section

Materials. 6-Bromohexan-1-ol (97%), 4,4′-biphenyldiol (97%), 1-dodecyne (98%), 1-tetradecyne (>95%), 1-hexadecyne (>95%), acryloyl chloride (98%), copper(II) acetate (98%), pentynoic acid (95%), *N*,*N*-dicyclohexylcarbodiimide (DCC, 99%), and *N*,*N*-(dimethylamino)pyridine (DMAP, 99%) were purchased from Aldrich and used without further purification. Tetrahydrofuran was dried over sodium metal and distilled. Other reagent-grade solvents were used as-received.

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-300 and Avance 500 spectrometer. FT-IR spectra were obtained with Perkin-Elmer Spectrum GX I using KBr pellets. Elemental analysis was performed using a CE instrument EA 1110 analyzer. Fluorescence images were obtained using a Carl Zeiss-LSM510 confocal laser scanning microscope. Fluorescence measurements were performed using a Shimadzu RF-5301PC spectrofluorometer. UV−vis spectra were obtained with the use of a SCINCO S-3150. SEM images were obtained by using a JEOL JSM-6330F microscope. TEM images were taken by a JEM-2000EXII microscope at 200 keV. Gel permeation chromatography (GPC) was carried out with a Viscotek Model 250 equipped with a RI750F refractive index detector from Younglin Instrument Co., Ltd. Styragel HR 4E and Styragel HR 5E columns from Waters were used as GPC columns with a flow rate of 1 mL min^{-1} at 35 °C by using THF as an eluent. Approximate calibration of the column was accomplished by means of narrow molecular weight polystyrene standards. The differential scanning calorimetry (DSC) measurements were performed with a TA modulated DSC Q10 at scanning rate of 10 °C min^{-1}. Dynamic mechanical analysis (DMA) tests were performed on a DMA 2980 dynamic mechanical analyzer (TA instruments) with a two-point binding film (tension) at a frequency of 1 Hz and amplitude of 5 μm from −50 to 120 °C at a heating rate of 3 °C min^{-1}. The tensile properties were measured with a universal testing machine (Instron-5543) with a 1 kN load cell at a constant cross-head speed of 3 mm min^{-1}.

Synthesis of 4′-Hydroxy-4-hexyloxybiphenyl. To a solution of 4,4′-biphenyldiol (22.6 g, 121.2 mmol) in DMF (80 mL) were added potassium carbonate (9.2 g, 66.6 mmol), potassium iodide (catalytic amount), and 1-bromohexane (10.0 g, 60.6 mmol) dropwise. The reaction mixture was stirred for 5 h at 80 °C under nitrogen and allowed to cool to room temperature. The resulting solution was poured into distilled water (400 mL). The precipitate was isolated by filtration, washed thoroughly with distilled water, and dried ($MgSO_4$). The solids were dissolved in ethyl acetate. Insoluble solids were removed by filtration and the solvent was evaporated. The product was recrystallized from ethanol to give white crystals. Yield, 8.2 g (52%). ^1H NMR ($CDCl_3$, ppm): δ 7.46 (dd, overlap, Ar, 4H), 6.95−6.88 (dd, overlap, Ar, 4H), 4.69 (s, $-OH$, 1H), 4.02 (t, $J = 6.6$ Hz, $-ArOCH_2-$, 2H), 1.84−1.70 (t, $J = 6.6$ Hz, $-OCCH_2-$, 2H), 1.52−1.26 (m, $-CH_2-$, 6H), 0.90 (t, $J = 6.5$ Hz, $-CH_3$, 3H).

Synthesis of Methyl 4-Pentynoate. This compound was prepared according to our previous report.[33]

Synthesis of Methyl 6-Heptynoate. To a solution of 6-heptynoic acid (12.0 g, 103.1 mmol) and methanol (9.8 g, 305.8 mmol) in diethyl ether (15 mL) were added DCC (25.2 g, 122.3 mmol) and DMAP (1.2 g, 10.2 mmol). The reaction mixture was stirred for 6 h at room temperature under nitrogen. Insoluble solids were removed by filtration through silica gel and the solvent was removed by evaporation. The product was isolated by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/9) as eluents to give a colorless liquid. Yield, 15.2 g (69%). ^1H NMR ($CDCl_3$): δ 3.72 (s, $-OCH_3$, 3H), 2.37 (t, $J = 7.3$ Hz, $\equiv CCH_2$, 2H), 2.24 (t, $J = 7.0$ Hz, $-OCOCH_2-$, 2H), 2.00 (s, $\equiv CH$, 1H), 1.78−1.26 (m, $-CH_2-$, 4H). ^{13}C NMR ($CDCl_3$): δ 171.9, 82.3, 69.0, 51.5. IR (KBr, cm^{-1}): 3295, 2956, 2122, 1739, 1439, 1367, 1201, 1171, 1038, 986, 835, 651.

Synthesis of Methyl Heptadeca-4,6-diynoate. This compound was prepared according to our previous report.[33]

Synthesis of Methyl Nonadeca-4,6-diynoate. To a solution of methyl 4-pentynoate (0.8 g, 7.1 mmol) and 1-tetradecyne (2.8 g, 14.3 mmol) in pyridine/methanol (40/40 mL) was added copper(II) acetate (4.0 g). The reaction mixture was refluxed for 18 h under nitrogen and allowed to cool to room temperature. Insoluble solids were removed by filtration and the solvent was removed by evaporation. The product was isolated by column chromatography on silica gel using ethyl acetate and *n* -hexane (1/8) as eluents to give a yellowish liquid. Yield, 1.3 g (60%). ^1H NMR ($CDCl_3$): δ 3.70 (s, $-OCH_3$, 3H), 2.56 (tt, overlap, $-OCOCH_2CH_2-$, 4H), 2.24 (t, $J = 7.0$ Hz, $\equiv CCH_2$, 2H), 1.58−1.48 (m, $\equiv CCCH_2$, 2H), 1.43−1.26 (m, $-CH_2-$, 18H), 0.88 (t, $J = 6.4$ Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 172.2, 78.6, 75.1, 66.3, 65.2, 52.1, 33.1, 32.1, 29.9, 29.8, 29.7, 29.6, 29.4, 29.3, 29.1, 28.5, 22.9, 19.4, 15.3, 14.3. IR (KBr, cm^{-1}): 2926, 2855, 2260, 2160, 1744, 1437, 1366, 1199, 1169, 1051, 985, 833, 722. Anal. Calcd (in wt %) for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.54; H, 10.73.

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Synthesis of Methyl Henicosa-4,6-diynoate. This compound was prepared from methyl 4-pentynoate (1.1 g, 9.4 mmol) and 1-hexadecyne (4.2 g, 18.9 mmol) as described for methyl nonadeca-4,6-diynoate. The product was isolated by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/8) as eluents to give a yellowish liquid. Yield, 1.5 g (50%). ^{1}H NMR ($CDCl_3$): δ 3.70 (s, $-OCH_3$, 3H), 2.58 (tt, overlap, $-OCOCH_2CH_2-$, 4H), 2.26 (t, J = 7.0 Hz, $\equiv CCH_2$, 2H), 1.58−1.48 (m, $\equiv CCCH_2$, 2H), 1.39−1.26 (m, $-CH_2-$, 22H), 0.90 (t, J = 6.4 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 172.2, 78.6, 75.1, 66.3, 65.2, 52.1, 33.1, 32.1, 29.9, 29.8, 29.7, 29.6, 29.3, 29.0, 28.5, 22.9, 19.4, 15.3, 14.3. IR (KBr, cm^{-1}): 2926, 2855, 2260, 2160, 1744, 1437, 1366, 1199, 1169, 1051, 985, 833, 722. Anal. Calcd (in wt %) for $C_{22}H_{36}O_2$: C, 79.46; H, 10.91. Found: C, 79.19; H, 11.12.

Synthesis of Methyl Heptadeca-6,8-diynoate. This compound was prepared from methyl 6-heptynoate (4.0 g, 28.5 mmol) and 1-decyne (7.9 g, 57.1 mmol) as described for methyl nonadeca-4,6-diynoate. The product was isolated by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/8) as eluents to give a yellowish liquid. Yield, 4.0 g (51%). ^{1}H NMR ($CDCl_3$): δ 3.69 (s, $-OCH_3$, 3H), 2.37 (ttt, $-OCOCH_2$, $\equiv CCH_2$, 6H), 1.78−1.28 (m, $-CH_2-$, 16H), 0.92 (t, J = 6.8 Hz, $-CH_3$, 3H).

Synthesis of 4-Hydroxy-4′-[6-(acryloyloxy)hexyloxy]biphenyl (8). This compound was prepared according to our previous report.[33]

Synthesis of Heptadeca-4,6-diynoic Acid (9). This compound was prepared according to our previous report.[33]

Synthesis of Nonadeca-4,6-diynoic Acid (10). To a solution of nonadeca-4,6-diynoate (2.0 g, 6.6 mmol) in THF (60 mL) was added a solution of potassium hydroxide (0.6 g, 10.9 mmol) in ethanol/water (4/1, 100 mL). The reaction mixture was refluxed. After evaporation of THF and ethanol, the mixture was acidified to the pH 4−5. The precipitate was isolated by filtration and washed with water. The product was recrystallized from *n*-hexane to give white crystals. Yield, 1.7 g (91%). ^{1}H NMR ($CDCl_3$): δ 2.61 (tt, overlap, $-OCOCH_2CH_2-$, 4H), 2.24 (t, J = 7.1 Hz, $\equiv CCH_2$, 2H), 1.49 (m, $\equiv CCCH_2$, 2H), 1.39−1.26 (m, $-CH_2-$, 18H), 0.88 (t, J = 6.4 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 176.5, 78.8, 74.7, 66.5, 65.1, 33.0, 32.1, 29.9, 29.8, 29.7, 29.5, 29.3, 29.1, 28.5, 22.9, 19.4, 15.1, 14.3. IR (KBr, cm^{-1}): 2955, 2920, 2848, 1691, 1460, 1432, 1413, 1298, 1215, 1176, 926, 724. Anal. Calcd (in wt %) for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.77; H, 10.54.

Synthesis of Henicosa-4,6-diynoic Acid (11). This compound was prepared from methyl henicosa-4,6-diynoate (1.3 g, 3.9 mmol) as described for compound **10**. The product was recrystallized from *n*-hexane to give white crystals. Yield, 1.1 g (88%). ^{1}H NMR ($CDCl_3$): δ 2.64 (tt, overlap, $-OCOCH_2CH_2-$, 4H), 2.26 (t, J = 7.1 Hz, $\equiv CCH_2$, 2H), 1.55 (m, $\equiv CCCH_2$, 2H), 1.40−1.26 (m, $-CH_2-$, 22H), 0.91 (t, J = 6.4 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 176.5, 78.8, 74.7, 66.5, 65.1, 33.0, 32.1, 29.9, 29.9, 29.9, 29.8, 29.7, 29.5, 29.3, 29.1, 28.5, 22.9, 19.4, 15.1, 14.3. IR (KBr, cm^{-1}): 2955, 2920, 2848, 1691, 1460, 1432, 1413, 1298, 1215, 1176, 926, 724. Anal. Calcd (in wt %) for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76. Found: C, 79.53; H, 10.89.

Synthesis of Heptadeca-6,8-diynoic Acid (12). This compound was prepared from methyl heptadeca-6,8-diynoate (5.2 g, 18.7 mmol) as described for compound **10**. The product was isolated by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/3) as eluents and recrystallized from *n*-hexane to give white crystals. Yield, 4.1 g (85%). ^{1}H NMR ($CDCl_3$): δ 2.40 (ttt, $-OCOCH_2$, $\equiv CCH_2$, 6H), 1.78−1.27 (m, $-CH_2-$, 16H), 0.90 (t, J = 6.8 Hz, $-CH_3$, 3H).

Synthesis of 4-(Heptadecanoyloxy)-4′-hexyloxybiphenyl (1). To a solution of 4′-hydroxy-4-hexyloxybiphenyl (0.50 g, 1.8 mmol) and heptadecanoic acid (0.50 g, 1.8 mmol) in CH_2Cl_2 (30 mL) were added DCC (0.46 g, 2.2 mmol) and DMAP (0.05 g, 0.37 mmol), and the mixture was stirred for 6 h at room temperature under nitrogen. Insoluble solids were removed by filtration through silica gel. The solvent was removed in vacuo and the product was recrystallized from ethanol and *n*-hexane to give white solids. Yield, 0.5 g (58%). ^{1}H NMR ($CDCl_3$): δ 7.58 (dd, overlap, Ar, 4H), 7.18 (d, J = 17.3 Hz, COOAr, 2H), 6.99 (d, J = 6.7 Hz, $-OAr$, 2H), 4.05 (t, J = 6.6 Hz, $-ArOCH_2-$, 2H), 2.59 (t, J = 6.5 Hz, $-OCOCH_2-$, 2H), 1.85−1.73 (m, $-OCCH_2-$, $-OCOCCH_2CH_2-$, 4H), 1.58−1.29 (m, $-CH_2-$, 32H), 0.90 (t, J = 6.5 Hz, $-CH_3$, 6H). ^{13}C NMR ($CDCl_3$): δ 172.6, 159.0, 149.9, 138.8, 133.0, 128.3, 127.9, 122.0, 115.0, 68.3, 34.7, 32.2, 31.8, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 26.0, 25.2, 23.0, 22.8, 14.3. Anal. Calcd (in wt %) for $C_{35}H_{54}O_3$: C, 80.41; H, 10.41. Found: C, 80.77; H, 10.62.

Synthesis of 4-(Heptadecanoyloxy)-4′-[6-(acryloyloxy)hexyloxy]biphenyl (2). This compound was prepared from compound **8** (0.5 g, 1.5 mmol) and heptadecanoic acid (0.4 g, 1.5 mmol) as described for compound **1**. The product was isolated by column chromatography on silica gel using tetrahydrofuran and *n*-hexane (1/3) as eluents and then recrystallized from ethanol and *n*-hexane to give white solids. Yield, 0.6 g (69%). ^{1}H NMR ($CDCl_3$): δ 7.54 (dd, overlap, Ar, 4H), 7.13 (d, J = 17.3 Hz, COOAr, 2H), 6.96 (d, J = 6.7 Hz, $-OAr$, 2H), 6.38 (d, J = 8.8 Hz, $=CH$, 1H), 6.17 (dd, J = 10.4, 7.0 Hz, $=CH$, 1H), 5.83 (d, J = 10.4 Hz, $=CH$, 1H), 4.23 (t, J = 6.6 Hz, $-OCH_2$, 2H), 4.20 (t, J = 6.6 Hz, $-ArOCH_2-$, 2H), 2.59 (t, J = 6.5 Hz, $-OCOCH_2-$, 2H), 1.85−1.73 (m, $-OCCH_2-$, 6H), 1.58−1.29 (m, $-CH_2-$, 30H), 0.90 (t, J = 6.5 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 172.6, 166.5, 158.9, 149.9, 138.8, 133.0, 130.7, 128.8, 128.3, 127.9, 121.9, 115.0, 68.1, 64.7, 34.7, 32.1, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.8, 26.0, 26.0, 25.2, 22.9, 14.3. IR (KBr, cm^{-1}): 2919, 2851, 1745, 1728, 1634, 1607, 1498, 1411, 1290, 1200, 1000, 830, 807. Anal. Calcd (in wt %) for $C_{38}H_{56}O_5$: C, 76.99; H, 9.52. Found: C, 76.91; H, 9.70.

Synthesis of 4-(Heptadeca-4,6-diynoyloxy)-4′-[6-(acryloyloxy)-hexyloxy]biphenyl (3). This compound was prepared according to our previous report.[33]

Synthesis of 4-(Nonadeca-4,6-diynoyloxy)-4′-[6-acryloyloxy]-hexyloxy]biphenyl (4). This compound was prepared from compound **8** (0.7 g, 1.9 mmol) and compound **10** (0.6 g, 1.9 mmol) as described for compound **1**. The product was isolated by column chromatography on silica gel using tetrahydrofuran and *n*-hexane (1/6) as eluents and then recrystallized from ethanol and *n*-hexane to give white solids. Yield, 0.6 g (69%). ^{1}H NMR ($CDCl_3$): δ 7.58 (dd, overlap, Ar, 4H), 7.18 (d, J = 17.3 Hz, COOAr, 2H), 6.99 (d, J = 6.7 Hz, $-OAr$, 2H), 6.45 (d, J = 8.8 Hz, $=CH$, 1H), 6.19 (dd, J = 10.4, 7.0 Hz, $=CH$, 1H), 5.86 (d, J = 10.4 Hz, $=CH$, 1H), 4.23 (t, J = 6.6 Hz, $-OCH_2$, 2H), 4.05 (t, J = 6.6 Hz, $-ArOCH_2-$, 2H), 2.84 (t, J = 6.5 Hz, $-OCOCH_2-$, 2H), 2.76 (t, J = 7.3 Hz, $-OCOCCH_2-$, 2H), 2.28 (t, J = 7.0 Hz, $\equiv CCH_2$, 2H), 1.85−1.73 (m, $-OCCH_2-$, 4H), 1.58−1.29 (m, $-CH_2-$, 24H), 0.93 (t, J = 6.5 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 172.6, 166.5, 158.9, 149.9, 138.8, 133.0, 130.7, 128.8, 128.3, 127.9, 121.9, 115.0, 68.1, 64.7, 34.7, 32.1, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.8, 26.0, 26.0, 25.2, 22.9, 14.3. IR (KBr, cm^{-1}): 2919, 2851, 2262, 2145, 1745, 1728, 1634, 1607, 1498, 1411, 1290, 1200, 1000, 830, 807. Anal. Calcd (in wt %) for $C_{40}H_{52}O_5$: C, 78.39; H, 8.55. Found: C, 78.48; H, 8.70.

Synthesis of 4-(Henicosa-4,6-diynoyloxy)-4′-[6-acryloyloxy]-hexyloxy]biphenyl (5). This compound was prepared from compound **8** (1.0 g, 2.9 mmol) and compound **11** (0.9 g, 2.9 mmol) as described for compound **1**. The product was isolated by column chromatography on silica gel using tetrahydrofuran and *n*-hexane (1/6) as eluents to give white solids. Yield, 1.6 g (84%). ^{1}H NMR ($CDCl_3$): δ 7.58 (dd, overlap, Ar, 4H), 7.18 (d, J = 17.3 Hz, COOAr, 2H), 6.99 (d, J = 6.7 Hz, $-$OAr, 2H), 6.45 (d, J = 8.8 Hz, $=$CH, 1H), 6.19 (dd, J = 10.4, 7.0 Hz, $=$CH, 1H), 5.86 (d, J = 10.4 Hz, $=$CH, 1H), 4.23 (t, J = 6.6 Hz, $-OCH_2$, 2H), 4.05 (t, J = 6.6 Hz, $-ArOCH_2-$, 2H), 2.84 (t, J = 6.5 Hz, $-OCOCH_2-$, 2H), 2.76 (t, J = 7.3 Hz, $-OCOCCH_2-$, 2H), 2.28 (t, J = 7.0 Hz, $\equiv CCH_2$, 2H), 1.85$-$1.73 (m, $-OCCH_2-$, 4H), 1.58$-$1.29 (m, $-CH_2-$, 28H), 0.93 (t, J = 6.5 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 170.4, 166.5, 158.9, 149.7, 139.0, 133.0, 130.7, 128.8, 128.3, 127.9, 121.9, 115.0, 78.8, 74.6, 68.1, 66.7, 65.2, 64.7, 33.5, 32.1, 29.8, 29.7, 29.5, 29.4, 29.3, 29.0, 28.8, 28.5, 26.0, 26.0, 22.9, 19.4, 15.5, 14.3. IR (KBr, cm^{-1}): 2919, 2851, 2262, 2145, 1745, 1728, 1634, 1607, 1498, 1411, 1290, 1200, 1000, 830, 807. Anal. Calcd (in wt %) for $C_{42}H_{56}O_5$: C, 78.71; H, 8.81. Found: C, 78.50; H, 8.89.

Synthesis of 4-(Heptadeca-6,8-diynoyloxy)-4′-[6-(acryloyloxy)-hexyloxy]biphenyl (6). This compound was prepared from compound **8** (1.3 g, 3.8 mmol) and compound **12** (1.0 g, 3.8 mmol) as described for compound **1**. The product was isolated by column chromatography on silica gel using ethylacetate and *n*-hexane (1/6) as eluents to give white solids. Yield, 2.2 g (67%). ^{1}H NMR ($CDCl_3$): δ 7.55 (dddd, overlap, Ar, 4H), 7.18 (dd, J = 17.3 Hz, COOAr, 2H), 6.99 (dd, J = 6.7 Hz, $-$OAr, 2H), 6.45 (d, J = 8.8 Hz, $=$CH, 1H), 6.19 (dd, J = 10.4, 7.0 Hz, $=$CH, 1H), 5.84 (d, J = 10.4 Hz, $=$CH, 1H), 4.20 (t, J = 6.6 Hz, $-OCH_2$, 2H), 4.02 (t, J = 6.6 Hz, $-ArOCH_2-$, 2H), 2.63 (t, J = 6.5 Hz, $-OCOCH_2-$, 2H), 2.34$-$2.23 (tt, J = 7.0 Hz, $\equiv CCH_2$, 4H), 1.89$-$1.27 (m, $-CH_2-$, 24H), 0.90 (t, J = 6.5 Hz, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 170.4, 166.5, 158.9, 149.7, 139.0, 133.0, 130.7, 128.8, 128.3, 127.9, 121.9, 115.0, 78.8, 74.6, 68.1, 66.7, 65.2, 64.7, 33.5, 32.1, 29.8, 29.7, 29.5, 29.4, 29.3, 29.0, 28.8, 28.5, 26.0, 26.0, 22.9, 19.4, 15.5, 14.3. IR (KBr, cm^{-1}): 2919, 2851, 2262, 2145, 1745, 1728, 1634, 1607, 1498, 1411, 1290, 1200, 1000, 830, 807. Anal. Calcd (in wt %) for $C_{38}H_{48}O_5$: C, 78.05; H, 8.27. Found: C, 78.17; H, 8.41.

Synthesis of Ethyl 4-(4-Hydroxyphenyl)benzoate. To a solution of 4′-hydroxy-4-biphenylcarboxylic acid (10 g, 46.7 mmol) in ethanol (200 mL) was added a catalytic amount of sulfuric acid. The reaction mixture was vigorously stirred, heated under reflux for 24 h, and allowed to cool to room temperature. The resulting solution was evaporated, poured into cool water, and neutralized to pH 8. The precipitate was isolated by filtration and washed several times with water. The product was purified by recrystallization from ethanol. Yield, 11.3 g (99.8%). ^{1}H NMR ($CDCl_3$): δ 8.11 (d, J = 8.3 Hz, $-$OCOAr$-$, 2H), 7.62 (d, J = 8.3 Hz, Ar, 2H), 7.54 (d, J = 8.5 Hz, Ar, 2H), 6.98 (d, J = 8.0 Hz, Ar, 2H), 5.30 (s, $-$OH, 1H), 4.44 (t, $-COOCH_2-$, 2H), 1.44 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 165.6, 158.0, 144.6, 129.7, 129.4, 128.1, 127.6, 125.9, 115.9, 60.6, 14.2. IR (KBr, cm^{-1}): 3331, 3001, 2988, 1682, 1602, 1587, 1532, 1498, 1440, 1404, 1372, 1302, 1277, 1191, 1136, 1116, 1021, 833, 774. Anal. Calcd (in wt %) for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.19; H, 5.86.

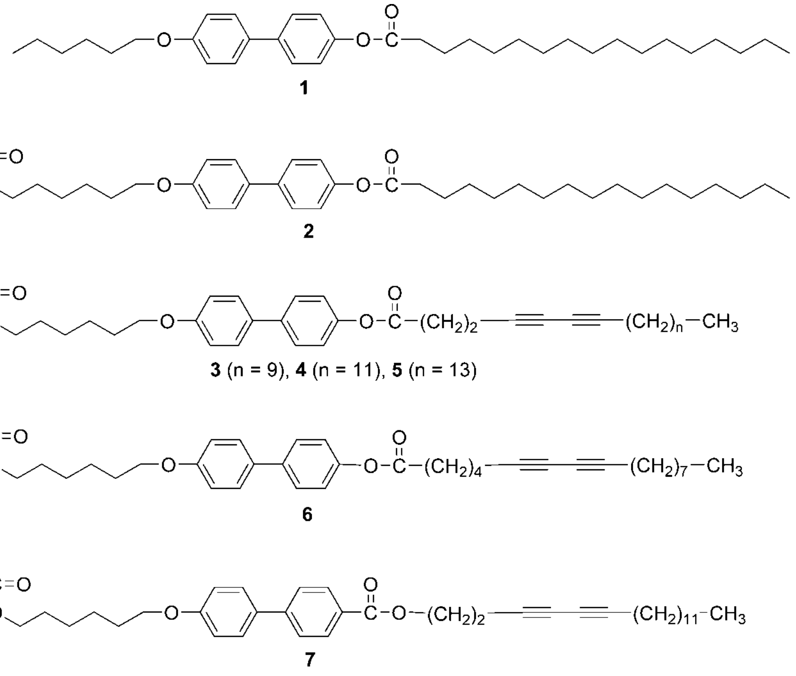
Synthesis of Ethyl 4-[4-(6-hydroxyhexyloxy)phenyl]benzoate. To a solution of ethyl 4-(4-hydroxyphenyl)benzoate (5.0 g, 20.6 mmol), potassium carbonate (3.7 g, 26.8 mmol), and a pinch of potassium iodide in DMF (50 mL) was added 1-bromo-6-hydroxyhexane (4.9 g, 26.8 mmol) dropwise. The reaction mixture was vigorously stirred at 80 °C for 48 h under nitrogen and allowed to cool to room temperature. The resulting solution was poured into distilled water (250 mL). The precipitate was isolated by filtration and washed several times with distilled water. The product was purified by recrystallization from ethanol. Yield, 7.0 g (99.1%). ^{1}H NMR ($CDCl_3$): δ 8.11 (d, J = 8.3 Hz, $-$OCOAr$-$, 2H), 7.62 (dd, overlap, Ar, 4H), 7.00 (d, J = 8.8 Hz, $-$OAr$-$, 2H), 4.44 (t, $-COOCH_2-$, 2H), 4.05 (t, $-OCH_2$, 2H), 1.87$-$1.40 (m, $-CH_2-$, 13H). ^{13}C NMR ($CDCl_3$): δ 166.8, 159.6, 145.4, 132.5, 132.5, 130.3, 128.8, 128.5, 126.6, 115.1, 68.2, 63.1, 61.1, 32.9, 29.4, 26.1, 25.8, 14.6. IR (KBr, cm^{-1}): 3315, 2935, 2860, 1713, 1604, 1528, 1498, 1470, 1400, 1369, 1288, 1254, 1197, 1109, 1029, 829, 772. Anal. Calcd (in wt %) for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.62; H, 7.66.

Synthesis of 4-[4-(6-Hydroxyhexyloxy)phenyl]benzoic acid. To a solution of ethyl 4-[4-(6-hydroxyhexyloxy)phenyl]benzoate (5.0 g, 14.6 mmol) in THF (30 mL) was added a solution of potassium hydroxide (1.6 g 29.2 mmol) in ethanol/water (5/1, 60 mL). The reaction mixture was vigorously stirred at reflux temperature for 12 h and allowed to cool to room temperature. The resulting solution was evaporated in vacuo and the residue was poured into distilled water. The precipitate was isolated by filtration and washed several times with distilled water. The product was purified by recrystallization from ethanol. Yield, 4.5 g (98.6%). ^{1}H NMR (DMSO-d_6): δ 7.86 (d, J = 7.9 Hz, $-$OCOAr$-$, 2H), 7.59 (d, J = 8.5 Hz, Ar, 2H), 7.47 (d, J = 8.1 Hz, Ar, 2H), 7.00 (d, J = 8.5 Hz, $-$OAr$-$, 2H), 4.36 (s, $-$OH, 1H), 4.02 (t, $-ArOCH_2-$, 2H), 3.45 (t, $-OCH_2$, 2H), 1.75$-$1.65 (m, $-OCCH_2-$, 4H), 1.54$-$1.27 (m, $-CH_2-$, 4H). ^{13}C NMR (DMSO-d_6): δ 166.8, 159.6, 145.4, 132.5, 130.3, 128.8, 128.5, 126.6, 115.1, 68.2, 63.1, 61.1, 32.9, 29.4, 26.1, 25.8, 14.6. IR (KBr, cm^{-1}): 3254, 2941, 2862, 1594, 1574, 1546, 1527, 1476, 1389, 1277, 1192, 1030, 830, 789. Anal. Calcd (in wt %) for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.39; H, 7.10.

Synthesis of 4-[4-(6-Acryloyloxyhexyloxy)phenyl]benzoic acid. To a solution of 4-[4-(6-hydroxyhexyloxy)phenyl]benzoic acid (5.0 g, 15.9 mmol), *N*,*N*-diethylaniline (2.0 g, 16.7 mmol), and a catalytic amount of 2,6-di-*tert*-butylphenol in 1,4-dioxane (50 mL) was added acryloylchloride (4.3 g, 47.7 mmol) dropwise. The reaction mixture was stirred at 25 °C for 24 h. The resulting solution was poured into cold water. The precipitate was isolated by filtration and washed several times with distilled water. The product was purified by recrystallization from ethanol: yield, 4.1 g (70.0%). ^{1}H NMR ($CDCl_3$): δ 8.17 (d, J = 8.4 Hz, $-$OCOAr$-$, 2H), 7.67 (d, J = 8.4 Hz, Ar, 2H), 7.59 (d, J = 8.7 Hz, Ar, 2H), 7.00 (d, J = 8.8 Hz, $-$OAr$-$, 2H), 6.44 (d, J = 17.3 Hz, $=$CH, 1H), 6.17 (dd, J = 10.4, 6.9 Hz, $=$CH, 1H), 5.84 (d, J = 10.4 Hz, $=$CH, 1H), 4.21 (t, $-OCH_2-$, 2H), 4.04 (t, $-ArOCH_2-$, 2H), 1.84$-$1.70 (m, $-OCCH_2-$, 4H), 1.60$-$1.47 (m, $-CH_2-$, 4H). ^{13}C NMR ($CDCl_3$): δ 166.6, 159.7, 146.4, 132.3, 131.0, 130.8, 128.8, 128.6, 126.8, 115.2, 104.8, 68.1, 64.7, 29.4, 28.8, 26.0. IR (KBr, cm^{-1}): 2938, 2865, 1724, 1694, 1678, 1635, 1604, 1431, 1409, 1292, 1248, 1194, 1009, 985, 832, 810, 774. Anal. Calcd (in wt %) for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.77; H, 6.72.

Synthesis of Octadeca-3,5-diyn-1-ol. To a solution of 3-butyn-1-ol (4.0 g, 40.8 mmol) and 1-tetradecyne (11.9 g, 61.1 mmol) in pyridine/methanol (80/80 mL) was added copper(II) acetate (14.8 g, 81.6 mmol). The reaction mixture was vigorously stirred at 60 °C for 18 h under nitrogen. Insoluble solids were removed by filtration. After evaporation of the solvent, the product was isolated as an oil by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/3) as eluents. Yield, 7.0 g (46.2%). ^{1}H NMR ($CDCl_3$): δ 3.69 (t, $-OCH_2$, 2H), 2.34 (m, $\equiv CCH_2$, 4H), 1.70$-$1.41 (m, $-CH_2-$, 20H), 0.94 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 78.0, 77.0, 65.9, 65.3, 62.5, 32.1, 32.0, 29.9, 29.7, 29.3, 29.1, 28.5, 24.8, 22.9, 19.4, 19.2, 14.3. IR (KBr, cm^{-1}): 3334, 2933, 2873, 2257, 2166, 1456, 1425, 1323, 1254, 1060, 980, 936. Anal. Calcd (in wt %) for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.04; H, 11.63.

Scheme 1. Biphenyl Esters Studied as Potential Organogelators



Synthesis of Octadeca-3,5-diynyl 4-[4-(6-Acryloyloxyhexyloxy)phenyl]benzoate (7). To a solution of 4-[4-(6-acryloyloxyhexyloxy)phenyl]benzoic acid (1.3 g, 3.4 mmol) and octadeca-3,5-diyn-1-ol (0.9 g, 3.4 mmol) in CH_2Cl_2 and THF (20/20 mL) were added DCC (0.8 g, 4.1 mmol) and DMAP (0.09 g, 0.68 mmol). The reaction mixture was stirred at room temperature for 24 h. After filtration and evaporation, the product was isolated as solid powders by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluents. Yield, 1.2 g (59.3%). ^{1}H NMR ($CDCl_3$): δ 8.10 (d, $J = 8.3$ Hz, $-OCOAr-$, 2H), 7.63 (dd, overlap, Ar, 4H), 7.00 (d, $J = 8.8$ Hz, $-OAr-$, 2H), 6.44 (d, $J = 17.3$ Hz, $=CH$, 1H), 6.17 (dd, $J = 10.3$, 7.0 Hz, $=CH$, 1H), 5.84 (d, $J = 10.3$ Hz, $=CH$, 1H), 4.43 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.00 (t, $-ArOCH_2-$, 2H), 2.77 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.83−1.70 (m, $-OCCH_2-$, 4H), 1.53−1.25 (m, $-CH_2-$, 24H), 0.93 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$): δ 166.6, 166.5, 159.6, 145.6, 132.5, 130.7, 130.3, 128.8, 128.6, 128.5, 126.6, 115.1, 78.1, 76.7, 68.1, 66.1, 65.3, 64.7, 64.5, 32.1, 29.9, 29.7, 29.5, 29.4, 29.3, 29.1, 28.8, 28.5, 28.1, 26.0, 25.2, 19.4, 19.2, 14.2. IR (KBr, cm^{-1}): 2935, 2854, 2243, 2145, 1736, 1723, 1634, 1606, 1408, 1000, 985, 875, 844, 810. Anal. Calcd (in wt %) for $C_{40}H_{52}O_5$: C, 78.39; H, 8.55. Found: C, 78.15; H, 8.62.

Radical Polymerization of HMA. In a 20 mL polymerization tube, hexyl methacrylate (5 g, 29.39 mmol) and AIBN (0.05 g, 0.29 mmol) were dissolved in anisole (10 mL). After three freeze−thaw cycles under nitrogen, the tube was sealed and placed in an oil bath at 60 °C for 24 h with stirring. The polymer was precipitated in ethanol and purified by reprecipitation of the polymer solution in THF into ethanol. Yield, 50.7%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.15−6.9 (8H, Ar−H), 4.22−2.35 (6H, $-OCH_2$, $\equiv CCH_2$), 1.82−1.25 (m, 19H, polymer backbone and alkyl chain protons), 0.83 (3H, $-CH_3$).

Results and Discussion

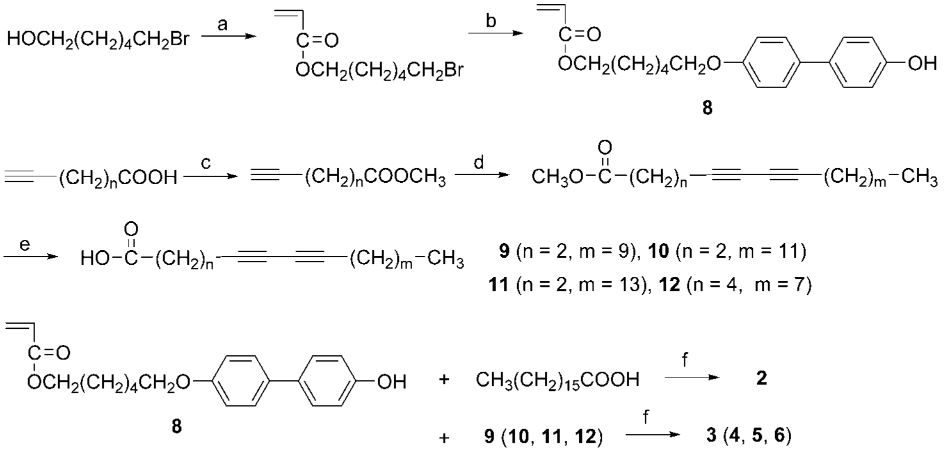
Scheme 1 shows the series of biphenyl esters studied in this work as potential organogelators. Biphenyl esters have been widely used as the building blocks of mesogenic compounds because of their structural simplicity and ease of derivatization. The biphenyl esters designed for a gelator consisted of a rigid biphenyl group, long hydrocarbon tails, and one or two polar ester bonds. By varying the structures of the attached groups, we were able to control the polarizability and the balance between the hydrophobicity and hydrophilicity of the compounds. We first investigated the gelation ability of a simple biphenyl ester (**1**) having a hexyloxy and a hexadecyl group at both its ends. The compound was synthesized by the reactions of 4,4′-biphenyldiol with hexyl bromide and then with hexadecanoic acid. Compound **1** showed the ability to gelate the following common organic solvents at room temperature: decane, cyclohexane, acetonitrile, methanol, and ethanol (Table 1). The critical gelation concentration was 0.1 wt % in decane. Monomeric solvents such as methyl methacrylate (MMA), hexyl methacrylate (HMA), and acrylonitrile (AN) were also gelated by compound **1**. Next, we prepared a polymerizable gelator (**2**) by introducing an acryl group at the end of the hexyloxy tail. 4,4′-Biphenyldiol was reacted with acryloylhexylbromide and then esterified with hexadecanoic acid to give compound **2**. Compound **2** showed a similar gelation ability to compound **1**. This result was very encouraging since the presence of an additional polar ester bond often

Table 1. Gelation Test Results of Compounds 1−5 at a concentration of 1.5 wt %

solvent	1	2	3	4	5
cyclohexane	G	G	G	G	G
decane	G	G	G	G	G
DMF	G	G	G[a]	G[a]	G
methanol	G	G	G	G	G
ethanol	G	G	G	G	G
ethyl acetate	G	G	G[a]	G[a]	G[a]
toluene	G[a]	G[a]	S	S	S
hexyl methacrylate	G	G	G[a]	G[a]	G
methyl methacrylate	G	G	G[a]	G[a]	G[a]
acrylonitrile	G	G	G[a]	G[a]	G

[a] At a concentration of 10 wt %. G, gel; S, solution.

Scheme 2. Synthesis of Heterobifunctional Gelators (3−6)[a]



[a] (a) Acryloyl chloride, TEA, THF, 0 °C; (b) 4,4′-biphenyldiol, K_2CO_3, DMF, 60 °C; (c) methanol, DCC, DMAP, diethyl ether, r.t.; (d) 1-alkyne, pyridine, methanol, copper(II) acetate, reflux; (e) H_2O, KOH, ethanol, THF, reflux; (f) DCC, DMAP, CH_2Cl_2, r.t.

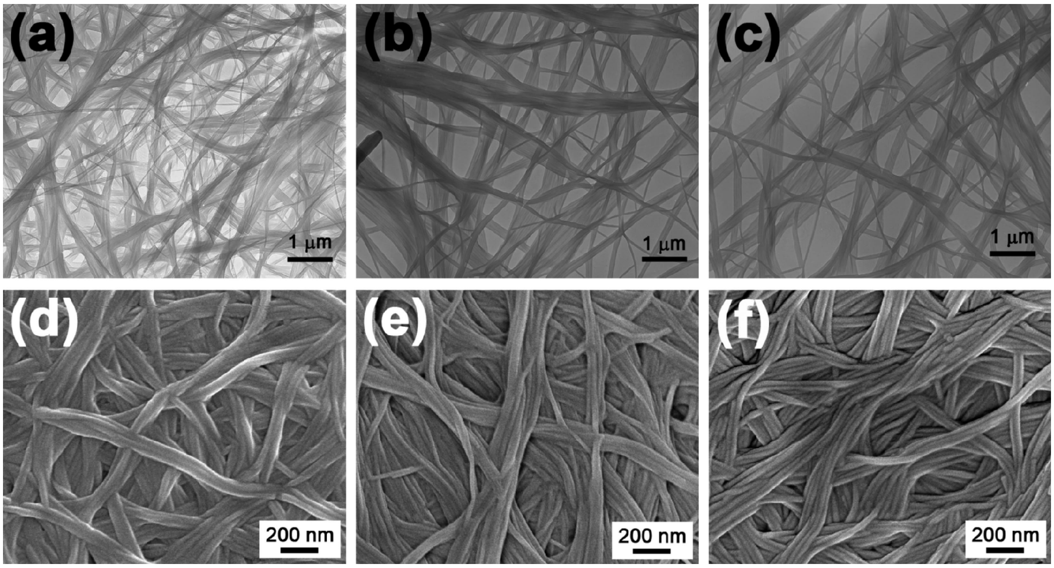


Figure 1. TEM (a−c) and SEM (d−f) images of the dried gels of **3** (a, d), **4** (b, e), and **5** (c, f). For the TEM and SEM measurements, the gels were prepared in decane and in methanol, respectively. The gelator concentration was 1.5 wt %.

disturbs the balance between the hydrophobicity and hydrophilicity of the compound, thereby preventing its aggregation.

We introduced a second polymerizable group into the biphenyl ester gelator. Compounds **3**−**7**, having two polymerizable groups, namely, an acryl and a diacetylene group, were synthesized according to Scheme 2. Hydroxybiphenyl having an acryl group (**8**) was prepared using our previously reported method.[33] Diynoic acids (**9**−**12**) were prepared by the coupling reaction of methyl 1-pentynoate or methyl 1-heptynoate with 1-alkyne, and subsequent hydrolysis. Esterification reactions of compound **8** and carboxylic acids **9**−**12** were carried out by using DCC in methylene chloride to yield compounds **3**−**7**. These compounds have heterobifunctionality due to the different photoreactivities of the acryl and diacetylene groups.

Compounds **3**−**5** formed stable organogels in organic solvents including decane, cyclohexane, acetonitrile, methanol, and ethanol at a concentration of 1.5 wt %. However, in ethyl acetate and MMA stable organogels formed only at higher concentrations. This suggests that the presence of a rigid diacetylene group in the hydrocarbon tail had an adverse effect on the gelation. Compounds **6** and **7** did not form a stable gel in any organic solvent despite their structural similarities to compounds **3**−**5**. Compound **6** had a butyl spacer between the biphenylester and the diyne groups, which was longer than the ethyl spacer of compounds **3**−**5**. In compound **7**, the diacetylene group was connected to the biphenyl group via an ester bond having an inverse direction to those in compounds **3**−**5**.

Figure 1 shows the TEM and SEM images of the dried organogels of compounds **3**−**5**. The gels formed in decane were dried on a carbon-coated copper grid. TEM showed the presence of entangled fibers with diameters ranging from 50 to 200 nm. When the gels formed in methanol were freeze-dried, much denser fibrous network structures were observed by SEM.

The polymerization of organogels of heterobifunctional gelators **3**−**5**, formed in the monomeric solvent HMA, was investigated in detail. Compound **5** formed a stable gel in HMA at room temperature, whereas compounds **3** and **4**

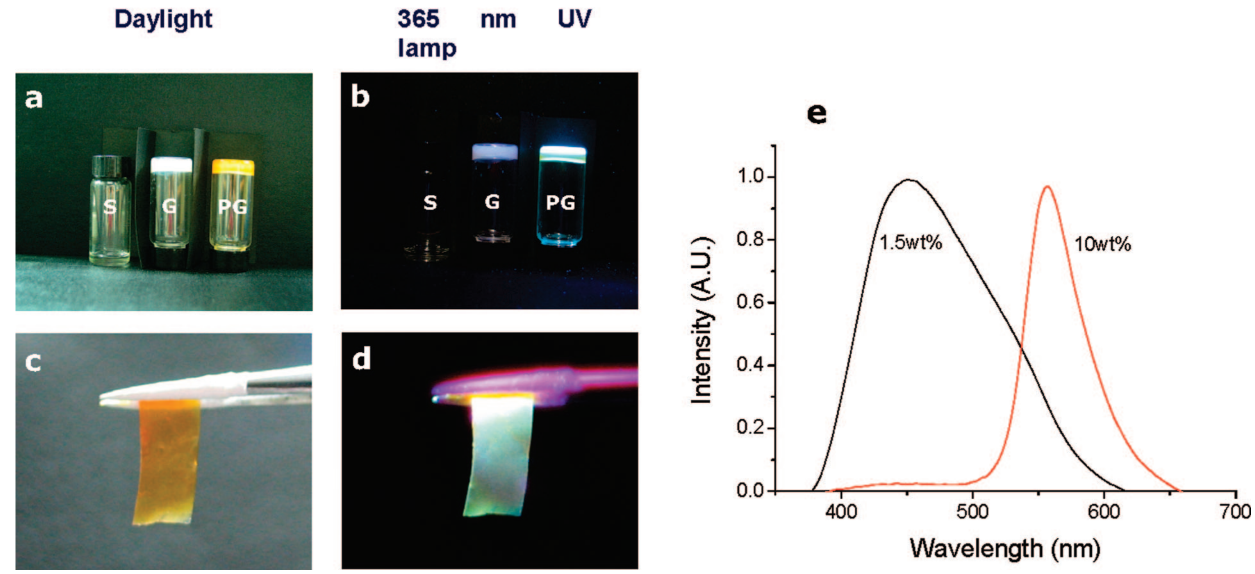


Figure 2. Photographs of vials containing a sol in decane at 50 °C (left), a gel in decane at room temperature (middle), and a polymerized gel in HMA (right) of compound **3** (1.5 wt %), which were taken (a) during daylight irradiation and (b) during irradiation using a 365 nm UV light in the dark. Photographs of the free-standing film of the polymerized gel (10 wt %), which were taken (c) during daylight irradiation and (d) during irradiation using a 365 nm UV light in the dark. (e) Photoluminescence spectra of the polymerized gels (1.5 and 10 wt %) (365 nm excitation).

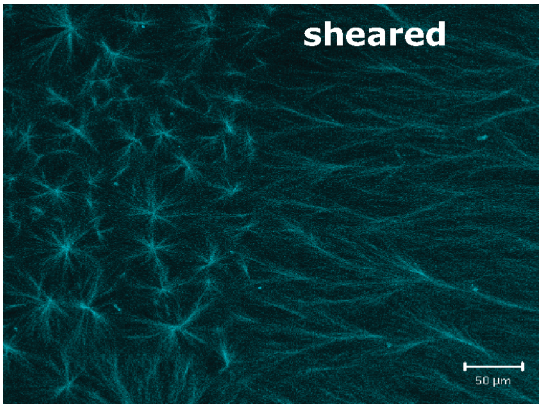


Figure 3. CLSM image of the polymerized gel (10 wt %) of **5** (scale bar: 50 *μ*m).

formed stable gels only below 13 °C, all at a concentration of 1.5 wt %. The longer alkyl tail of compound **5** (relative to compounds **3** and **4**) seemed to have a favorable effect on the formation of a stable gel. The organogels of compounds **3**−**5** (1.5 or 10 wt %) formed in HMA were polymerized in the presence of 2,2-dimethoxy-2-phenylacetophenone (photoinitiator, 4 wt %) by photoirradiation with a UV lamp (a high-pressure mercury arc lamp 3 mW/cm^2) for 48 h at 0 °C.

Figure 2a shows photographs of the sol (in decane at 50 °C), the gel (in decane at room temperature), and the polymerized gel (in HMA) of compound **3**, which were taken during daylight irradiation. The polymerized gel appeared yellowish because of the presence of polydiacetylene chains with relatively short conjugation lengths. When irradiated with 365 nm UV light, the polymerized gel exhibited strong fluorescence [Figure 2b]. The gelator in the sol state did not show fluorescence, but after gelation it became fluorescent. This was attributed to the conformational change of the gelator caused by the aggregation. An “aggregation-induced fluorescence” has been observed in the self-assembly of various aromatic compounds.[34–36] In a solution, the biphenyl group of compound **3** would have a nonplanar conformation with a certain dihedral angle.[37] When compound **3** aggregated, a partial coplanarization could be induced, leading to a better conjugation between two phenyl rings.

Parts (c) and (d) of Figure 2 show photographs of free-standing films (approximately 50 *μ*m thick) obtained by the polymerization of the organogel of compound **3** (10 wt %) in HMA. The film also showed fluorescence upon irradiation with a 365 nm UV light. The photoluminescence spectrum of the polymerized gel was very dependent on the concentration of the gelator [Figure 2e]. The polymerized gel of compound **3** (1.5 wt %) showed an emission maximum at 450 nm when excited at 365 nm. When the concentration of the gelator was increased to 10 wt %, the fluorescence peak was significantly red-shifted with an emission maximum at 550 nm, suggesting the formation of a polydiacetylene chain having a longer conjugation length.

Since the fluorescence came from polydiacetylene chains comprising the nanofibers of the polymerized gels, we were able to visualize the nanofibers embedded in the polymer matrix by using a confocal laser scanning microscope (CLSM). A mixture of a heterobifunctional gelator (10 wt %) and 2,2-dimethoxy-2-phenylacetophenone (4 wt %) in HMA was sandwiched between two glass substrates, at 0 °C, and exposed to UV light for 24 h (using a high-pressure mercury lamp, 3 mW/cm^2). The CLSM images of the films were obtained by using the 458 nm line of an argon-ion laser for excitation and detecting the emission above 475 nm. Fluorescent nanofibers dispersed in the polymer matrix can

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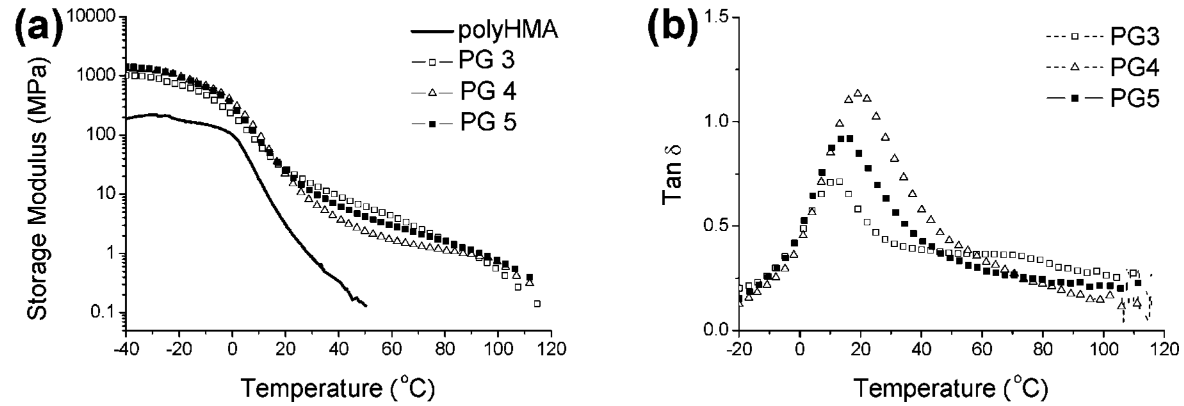

Figure 4. DMA results: (a) storage modulus versus temperature and (b) tan δ versus temperature for polyHMA and polymerized gels of **3**−**5** (**PG 3**−**5**).

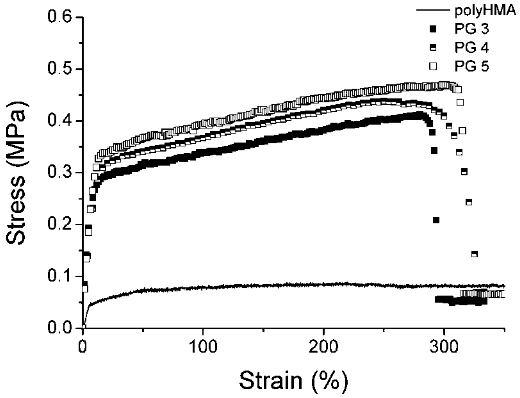

Figure 5. Stress−strain curves for the polymerized films and polyHMA.

Table 2. Mechanical Properties of the Polymerized Gels (PG 3−5, 10 wt %) **and polyHMA**

sample	Young's modulus (MPa)	tensile strength (MPa)	elongation at break
PG 3	4.4 ± 1.0	0.4 ± 0.1	≈300 ± 30
PG 4	3.2 ± 0.8	0.4 ± 0.1	≈310 ± 30
PG 5	4.1 ± 1.0	0.5 ± 0.1	≈310 ± 30
polyHMA	1.0 ± 0.3	0.08 ± 0.03	>1000

be clearly seen in Figure 3. The fibers are homogeneously distributed in the film. We were even able to align the nanofibers by shearing the organogels before the polymerization.

The polymerization of an organogel consisting of a heterobifunctional gelator and a monomeric solvent has an important advantage for the preparation of a nanofiber reinforced composite in terms of producing a fine distribution of nanofibers in a polymer matrix. In the gel state, the nanofibers formed by noncovalent interactions of the gelator molecules were surrounded by monomeric solvent molecules. We presume that the polymerization could occur via four different pathways. The UV irradiation of the gels could initiate the polymerization of an acryl group of HMA with the aid of a photoinitiator to form a polymer matrix. An acryl group of the gelator could also be polymerized inside the nanofibers or copoymerized with HMA at the interface between the nanofibers and HMA. At the same time the polymerization of a diacetylene group of the gelator could occur, leading to the nanofibers having a cross-linked structure.

We investigated the reinforcing effects of the polymerized gelator fibers on the matrix polymer, polyHMA. The polymerized gels showed much improved thermal and physical properties compared to those of polyHMA. PolyHMA was prepared by radical polymerization with AIBN in anisole at 60 °C for 24 h. The number and weight average molecular weights, measured by GPC, were 45000 and 94000, respectively. In the DSC trace of polyHMA obtained at a heating rate of 10 °C min^{-1}, a glass transition was observed at −5 °C. The breadth of the glass transition was noticeably broad (25 °C), which is in agreement with a previous report.[38] In contrast, the polymerized gel did not show any distinct transitions in the DSC trace.

More information could be collected by dynamic mechanical analysis (DMA). A polyHMA film (approximately 500 μm thick) was fabricated by casting a polymer solution in chloroform onto a glass plate. The polymerized gel films were prepared by the photopolymerization of the organogels containing 10 wt % of an organogelator in HMA in the presence of a photoinitiator. The films were placed in the tension clamp of the calibrated instrument and then heated from −50 to 120 °C at a heating rate of 3 °C min^{-1}. The storage modulus (G'), loss modulus (G''), and tan δ values were measured at a constant frequency (1 Hz) in air. The tan δ value, which is a ratio G''/G', reaches its maximum at the glass-transition temperature (T_g) of the polymer. Figure 4 shows the dependence of the storage modulus and the tan δ values on the temperature for polyHMA and the polymerized gels of compounds **3**−**5**. As expected, the polymerized gels showed higher storage modulus values than polyHMA. The improved thermal stability was also witnessed for the polymerized gels in comparison to that of polyHMA. The storage moduli of the polymerized gels increased by more than 500% in comparison to that of polyHMA [Figure 4a]. The T_g values of the polymerized gels determined from the tan δ curve as a function of temperature were around 20 °C. In contrast, it was difficult to obtain the tan δ curve of polyHMA due to the fluctuation of the values over 10 °C. The film fractured on reaching approximately 40 °C.

The tensile properties of the polymerized gel films (**PG 3**−**5**) and the polyHMA film were measured with a universal

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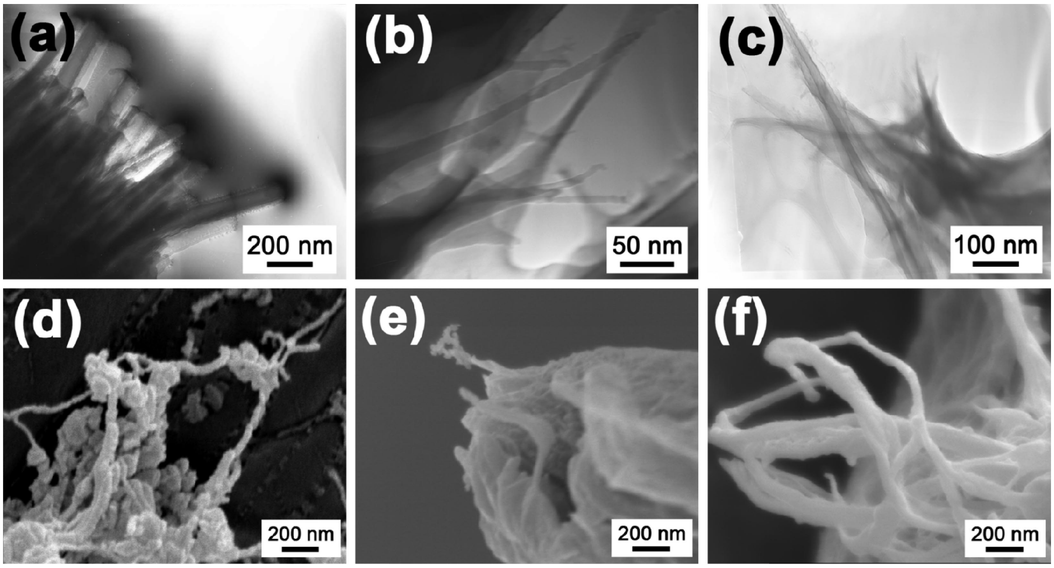

Figure 6. TEM (a−c) and SEM (d−f) images of nanofibers found at the cleaved edges of the polymerized gel films [**PG 3** (a, d), **PG 4** (b, e), and **PG 5** (c, f)].

testing machine, using a 1 kN load cell at a constant crosshead speed of 3 mm min^{-1}. The stress−strain curves of both films are shown in Figure 5, and their mechanical properties are listed in Table 2.

Both the Young's modulus and the tensile strength values of the polymerized gel films were significantly higher than those obtained for the polyHMA film. The addition of 10 wt % of the heterobifunctional gelator led to a nearly 4-fold increase in both the Young's modulus and the tensile strength of polyHMA. This suggests that the nanofibers, formed by polymerization of the gelator, were finely distributed in the polymer matrix, thereby reinforcing the structure. This was also corroborated by the TEM and SEM studies.

Figure 6 shows TEM and SEM images of the embedded fibers in polyHMA matrixes. The films were uniaxially extended at room temperature until they fractured. The projecting nanofibers with diameters ranging from 10 to 100 nm were found at the cleaved edge. We presume that the in situ photopolymerization of the polymerizable gelators in the monomeric solvent prevented further aggregation of the fibers, thereby enabling them to maximally interact with the polymer matrix.

Conclusions

We explored the use of a heterobifunctional organogelator having two different photopolymerizable groups for the fabrication of a polymeric nanocomposite. We prepared the organogels of the heterobifunctional organogelator in a monomeric solvent and polymerized them in the gel state. The polymerization occurred in the bulk of the monomeric solvent, inside the nanofibers assembled from the gelator molecules, and at the interface between the nanofibers and the solvent. The resulting polymeric nanofibers were evenly embedded in the polymer matrix, thereby reinforcing the structure. In particular, the polymerization at the interface likely improved the adhesion between the fiber and the polymer matrix. The approach described herein can be used for the synthesis of advanced nanocomposite materials.

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