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Composite Polymer Materials Consisting of Nanofilms Formed by Click Reaction between Polymers at an Oil–Water Interface

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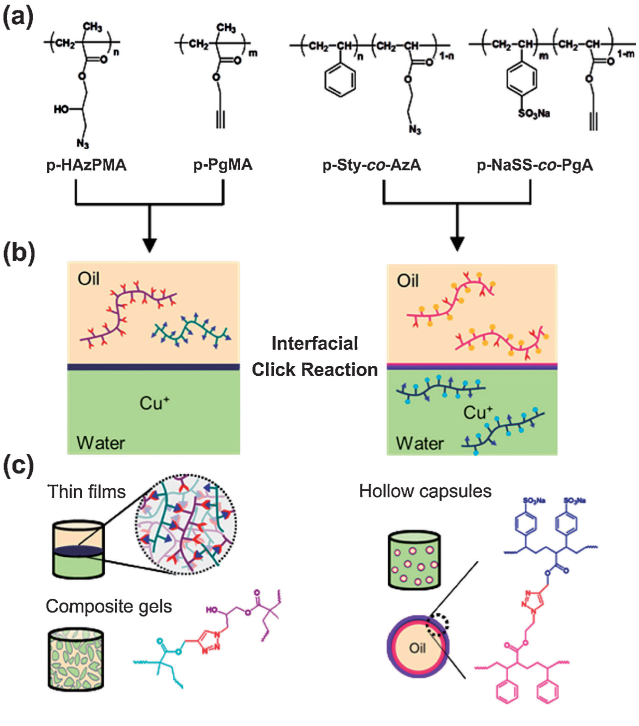
New polymer materials, including thin films, soft gels, and hollow capsules, consisting of composite polymer nanofilms were prepared by the Cu(I)-catalyzed Huisgen click reaction between lipophilic polymers or between lipophilic and hydrophilic polymers. Because the lipophilic polymer, or hydrophilic polymer and copper catalyst were present in the oil or aqueous phase, respectively, the crosslinking reaction proceeded only at the phase interface. The combination of lipophilic and hydrophilic polymers produced "Janus" nanofilms with both hydrophilic and lipophilic surfaces.

Recently, much attention has been directed at application of Sharpless "click" reactions,[1] because of the unique potential of this reaction to give high selectivity and high efficiency under mild reaction conditions without producing by-products. Various hierarchical nanostructured polymers, such as block polymers,[2] polymer gel networks,[3] and modified dendrimers[4] have been synthesized using the click reaction. Very recently, the click reaction has been conducted not only in homogeneous media but also at solid–liquid[5] and liquid–liquid (L/L) interfaces.[6] Stoddart and co-workers[7] have reported a unique selective click reaction at a liquid–solid interface induced by catalysis on the apex of an atomic force microscope tip. Polycondensation of adipoyl chloride and hexamethylenediamine is a classic example of a thin film constructed at a L/L interface.[8] Polymer thin films prepared by layer-by-layer techniques at emulsion[9] and macroscopic L/L interfaces[10] have also been reported.

In this communication, we report a simple click reaction between polymers at macroscopic oil–water interfaces in two phase solutions, oil-in-water (O/W) or water-in-oil (W/O) droplets, and use mechanical emulsions to construct new polymer materials based on nanofilms consisting of crosslinked polymers. Recently, Rotello and co-workers[6] have used a click reaction between polymer particles at a L/L interface to fabricate magnetic colloidal particles.

Among the reported click reactions, copper-catalyzed azide–alkyne cycloaddition, also known as the Huisgen click reaction, is the most popular and widely used.[11] Click reaction requires the coexistence of alkyne and azide units and a copper ion as a catalyst in the reaction phase. Therefore, when all three components were arranged separately in aqueous and oil phases, polymer–polymer crosslinking was expected to occur at the L/L interface.

To confirm the feasibility of interfacial click reaction taking place at an oil–water interface, three lipophilic and one hydrophilic polymer bearing an alkyne group, poly(2-hydroxy-3-azidopropyl methacrylate) (p-HAzPMA), poly(styrene-*co*-2-azidoethyl acrylate) (p-Sty-*co*-AzA), poly[propargyl (2-propynyl) methacrylate] (p-PgMA), and poly(sodium styrenesulfonate-*co*-propargyl acrylate) (p-NaSS-*co*-PgA), were synthesized by thermal radical polymerization (Scheme 1a). The purification of the polymers, except water-soluble p-NaSS-*co*-PgA, was conducted by reprecipitation and average molecular weights were evaluated by size exclusion chromatography in THF using polystyrene standards.[12]



Scheme 1. Chemical structures of the polymers used (a) and schematic representation of liquid–liquid (L/L) interfacial click reaction for homo- and hetero-type reactions (b) and products (c).

Poly(glycidyl methacrylate) (p-GMA, $M_w = 30300$) was prepared by thermal polymerization of glycidyl methacrylate by azobisisobutyronitrile (AIBN) in tetrahydrofuran (THF).[13] The epoxy units in p-GMA were reacted with NaN_3 and NH_4Cl in dimethylformamide (DMF) to synthesize p-HAzPMA by introducing azide units.[14,15] ^1H NMR spectroscopy revealed that the conversion ratio to azide units was 92 mol %. In the synthesis of p-PgMA ($M_w = 30400$), propargyl methacrylate monomer, which was prepared by reaction of methacryloyl chloride and propargyl alcohol with triethylamine, was polymerized in THF using AIBN.[16] After copolymerization between styrene and 2-bromoethyl acrylate (BrA) synthesized from acryloyl chloride and 2-bromoethanol, p-Sty-*co*-AzA ($M_w = 11400$) was synthesized by reaction of the copolymer with NaN_3 in DMF to convert bromide to azide units. BrA units in the copolymer

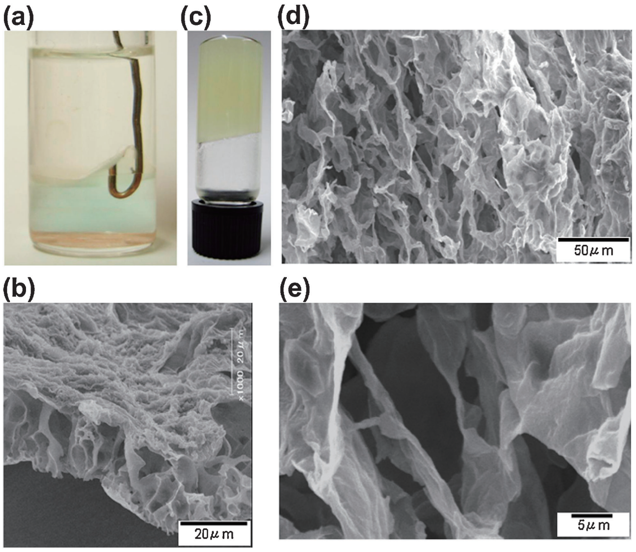


Figure 1. Photographs (a and c) and scanning electron microscopy images (b, d, and e) of water/ethyl acetate solutions containing crosslinked interfacial thin films (a, b) and composite gels (c–e) consisting of p-HAzPMA and p-PgMA.

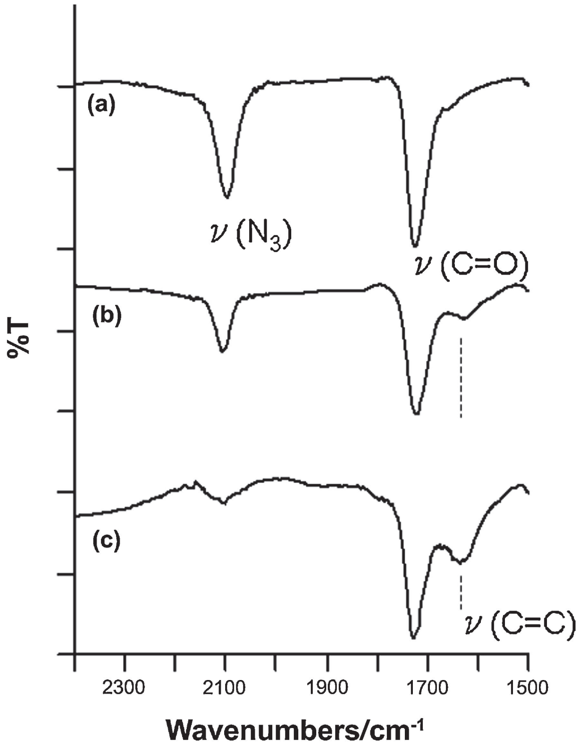


Figure 2. ATR-IR spectra of a simple mixture (1/1, w/w) (a), dried thin films formed at a macroscopic L/L interface (b) and dried composite gel (c) prepared from p-HAzPMA and p-PgMA.

before the conversion reaction and azide units in p-Sty-*co*-AzA were 15 and 11 mol% by ^{1}H NMR spectra and elemental analysis, respectively, indicating that the conversion ratio to azide units was 76 mol%.[17] Copolymerization of sodium styrene-sulfonate and propargyl acrylate (PgA)[18] in dimethyl sulfoxide with AIBN was conducted to prepare a hydrophilic copolymer bearing alkyne units, p-NaSS-*co*-PgA.[19] Purification was conducted by dialyzing entirely against deionized water using a dialysis bag (3500 MW cutoff). ^{1}H NMR spectra revealed that the molar ratio of PgA in the copolymer was 9.1 mol%.

Among the various polymers prepared, interfacial click reaction experiments conducted could be categorized into homo- and hetero-type reactions with two different polymer combinations, a lipophilic polymer and a lipophilic polymer, or a hydrophilic polymer and a lipophilic polymer, as shown in Schemes 1b and 1c. Highly crosslinked composite thin films consisting of lipophilic polymers formed at an O/W interface by click reaction between p-HAzPMA and p-PgMA. Interestingly, homointerfacial crosslinking click reaction between lipophilic polymers proceeded successfully only at a L/L interface, because the catalytic Cu ion was present only in aqueous solution.

Typically, a solution of p-HAzPMA (13 mM) and p-PgMA (20 mM) in ethyl acetate was gently poured into an aqueous solution of $CuSO_4$ (63 mM) and sodium ascorbate (85 mM) at room temperature. When the two phase solution was maintained at room temperature, thin films formed at the interface after one hour. Figure 1a shows a photograph of the solution containing a film at the interface after 13 h. The thin films were semi-transparent when wet after depositing on glass. The structure of the dried film was investigated by scanning electron microscopy (SEM) (Figure 1b). The typical thickness of the film was estimated to be several tens of μm. The film possessed a porous structure with closed cells. The cell walls were smooth and the thickness of walls was several hundred nm. The inside of each cell was filled with either water or oil. The formation mechanism of such a porous structure is unknown. The propagation of crosslinked polymers may influence the diffusion of the polymers and Cu ions, which leads to a complicated porous structure rather than a simple dense thin film because it may be a sort of dissipative structure.

When the O/W solution containing the polymers and Cu catalyst was shaken and heated slightly to accelerate the crosslinking reaction before formation of a thin film at the O/W interface and macroscopic separation of the solution, it was found that O/W composite soft gels formed,[20] as shown in Figure 1c. Figures 1d and 1e show typical SEM images of soft gel samples after freeze drying. Porous structures were observed. The cell wall consisted of smooth poreless films with a thickness of several hundred nm, essentially similar to the thin films formed at a macroscopic L/L interface. The typical volume ratio between water and ethyl acetate in the soft gel was 1/2. In the soft gels, water and oil domains might be separated by the cell wall.

The click reaction at a L/L interface was confirmed by ATR-IR measurements, as shown in Figure 2. A new peak at ca. 1630 cm^{-1}, which was attributed to the alkene bond of a triazole ring, appeared only after the click reaction (Figures 2b and 2c). This proves that the crosslinking click reaction proceeded at the L/L interface for both systems at a macroscopic interface and in a mechanical emulsion. Both the crosslinked products (thin film and soft gel) contained azide and alkyne units. The azide units in the polymers gave identical signals at ca. 2100 cm^{-1}. The percentage of reaction was evaluated as the reduction in the proportion of azide units using the change in the ratio between the azide and ester (at ca. 1725 cm^{-1}) peaks of the polymers. The

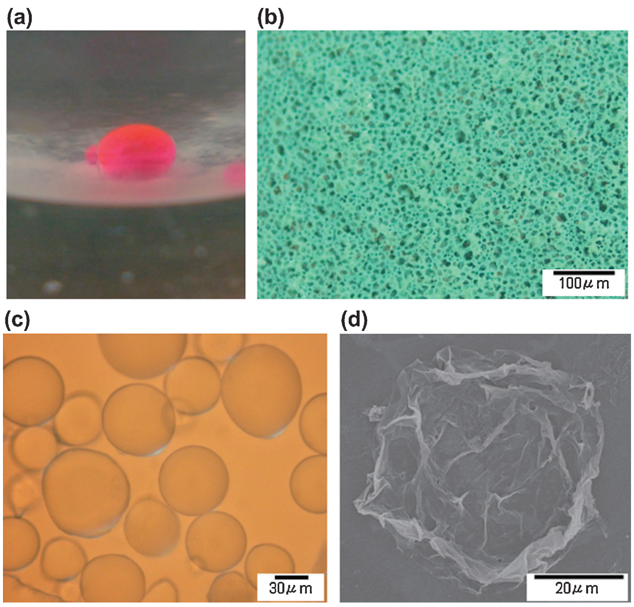


Figure 3. Photographic (a), normal optical microscope (b), optical polarization microscope (c), and SEM (d) images for hetero-crosslinked interfacial thin films (a and b) and O/W hollow capsules (c and d) consisting of p-Sty-*co*-AzA and p-NaSS-*co*-PgA.

percentage of reaction at the macroscopic L/L interface and in the mechanical emulsion was estimated to be ca. 28% and ca. 79%, respectively.

The heterointerfacial click reaction between lipophilic p-Sty-*co*-AzA (AzA units 11 mol %, azide concentration 5.0 mM) and hydrophilic p-NaSS-*co*-PgA (PgA units 9.1 mol %, alkyne concentration 2.1 mM) was also conducted across a L/L interface. Typically, an aqueous solution containing p-NaSS-*co*-PgA (5 mg mL^{-1}), sodium ascorbate (85 mM), and copper sulfate (63 mM), and solution of p-Sty-*co*-AzA (5 mg mL^{-1}) in ethyl acetate were prepared prior to the reaction. Ultrathin films consisting of p-NaSS-*co*-PgA and p-Sty-*co*-AzA spontaneously formed at a macroscopic L/L interface at 40 °C within an hour. The percentage of reaction at the macroscopic L/L interface was estimated to be ca. 40%.

Figure 3a shows a photograph of the two phase solution (lower aqueous and upper ethyl acetate phases) with a thin film at the interface after 3 h of reaction. In the photograph, a water droplet stained with Xylene Red was placed on the polymer film. The droplet was stable and did not fuse with the lower aqueous phase by passivation through the thin film. In addition, the spherical shape of the aqueous droplet indicates that the surface of the film facing the ethyl acetate solution was strongly hydrophobic.

The film was deposited on a glass plate, dried for a day in air, and then observed by optical microscope, as shown in Figure 3b. A homogeneous porous structure with pores of ca. 10 μm in diameter was observed. The pores might be formed by microseparation of the two phase solution. The porous structure was not smooth, possibly because it was a dissipative structure related to the hydrophilic–lipophilic balance of amphiphilic polymers formed by crosslinking.

When the crosslinking reaction of p-Sty-*co*-AzA and p-NaSS-*co*-PgA was conducted in a mechanical emulsion generated by shaking the solution, composite soft gels were not produced. Macroscopic separation occurred faster than immobilization by crosslinking because of the heavy specific gravity of $CHCl_3$. Instead, a heterointerfacial click reaction in an O/W emulsion was conducted. A solution of p-Sty-*co*-AzA (azide concentration: 10 mM) in $CHCl_3$ (100 μL) was added to an excess of an aqueous solution containing copper sulfate (63 mM), sodium ascorbate (85 mM), and p-NaSS-*co*-PgA (alkyne concentration: 4.2 mM). The mixture was vortexed and then allowed to stand at room temperature for one day. The aqueous solution was exchanged for pure water by rinsing. Surprisingly, stable $CHCl_3$ oil droplets with diameters of 10–60 μm formed in water, as shown in Figure 3c. SEM observation of the dried droplets revealed withered hollow capsules composed of poreless, smooth nanofilms (Figure 3d). This proves that the hydrophilic polymer in water and lipophilic polymer in oil crosslinked at a L/L interface by click reaction. It should be noted that such heterointerfacial click reactions provide "Janus" films with hydrophilic and lipophilic surfaces.

In conclusion, we have demonstrated that homo- and hetero-interfacial click reactions can be used to combine two polymers at L/L interfaces. Interfacial click reactions are able to produce a variety of polymer materials such as thin films, composite soft gels, and hollow capsules based on highly crosslinked polymer network systems. In particular, heterointerfacial reactions can produce nanohybrid polymer materials consisting of polymers possessing hydrophilic and lipophilic characteristics. The composite polymer materials produced by interfacial click crosslinking should have significant potential in a wide range of applications.

References and Notes

1 H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
2 W. Lin, Q. Fu, Y. Zhang, J. Huang, *Macromolecules* **2008**, *41*, 4127.
3 X.-D. Xu, C.-S. Chen, B. Lu, Z.-C. Wang, S.-X. Cheng, X.-Z. Zhang, R.-X. Zhuo, *Macromol. Rapid Commun.* **2009**, *30*, 157.
4 A. Vieyres, T. Lam, R. Gillet, G. Franc, A. Castonguay, A. Kakkar, *Chem. Commun.* **2010**, *46*, 1875.
5 T. Lummerstorfer, H. Hoffmann, *J. Phys. Chem. B* **2004**, *108*, 3963.
6 B. Samanta, D. Patra, C. Subramani, Y. Ofir, G. Yesilbag, A. Sanyal, V. M. Rotello, *Small* **2009**, *5*, 685.
7 W. F. Paxton, J. M. Spruell, J. F. Stoddart, *J. Am. Chem. Soc.* **2009**, *131*, 6692.
8 E. C. Botelho, N. Scherbakoff, M. C. Rezende, A. M. Kawamoto, J. Sciamareli, *Macromolecules* **2001**, *34*, 3367.
9 D. O. Grigoriev, T. Bukreeva, H. Möhwald, D. G. Shchukin, *Langmuir* **2008**, *24*, 999.
10 M. E. Buck, D. M. Lynn, *Adv. Mater.* **2010**, *22*, 994.
11 J. E. Hein, V. V. Fokin, *Chem. Soc. Rev.* **2010**, *39*, 1302.
12 All polymers were characterized by ^{1}H NMR. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
13 Y. Li, Y. Chen, C. Zhang, T. Xue, M. Yang, *Sens. Actuators, B* **2007**, *125*, 131.
14 N. V. Tsarevsky, S. A. Bencherif, K. Matyjaszewski, *Macromolecules* **2007**, *40*, 4439.
15 C. Li, Z. Ge, J. Fang, S. Liu, *Macromolecules* **2009**, *42*, 2916.
16 M. Munteanu, S. W. Choi, H. Ritter, *Macromolecules* **2008**, *41*, 9619.
17 G. K. Such, J. F. Quinn, A. Quinn, E. Tjipto, F. Caruso, *J. Am. Chem. Soc.* **2006**, *128*, 9318.
18 B.-Y. Zhang, W.-D. He, L.-Y. Li, X.-L. Sun, W.-T. Li, K.-R. Zhang, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 3604.
19 W. J. Bae, K. H. Kim, W. H. Jo, Y. H. Park, *Polymer* **2005**, *46*, 10085.
20 S. Kawano, D. Kobayashi, S. Taguchi, M. Kunitake, T. Nishimi, *Macromolecules* **2010**, *43*, 473.