Photogeneration of Gelatinous Networks from Pre-Existing Polymers

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ABSTRACT: In this manuscript we report the crosslinking of pre-existing macromolecules in solution through the use of photoactive benzophenone chromophores. We show that a bifunctional crosslinker composed of two benzophenone chromophores as well as a single benzophenone chromophore crosslink poly (butadiene) and poly (ethylene oxide) in solution to form insoluble gels when irradiated with UV light. The molecular weight between crosslinks of the photogenerated gels was compared for the two crosslinkers, for an equivalent amount of benzophenone chromophores in each solution, by measuring the swelling ratio of the gels formed. Gels formed from the bifunctional benzophenone crosslinker were shown to contain more than twice as many crosslinks compared to gels formed from the crosslinker composed of a single benzophenone chromophore. EPR measurements of a nitroxide derivative absorbed into the gels further supported a higher crosslink density for the gels formed from the bifunctional benzophenone crosslinker. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 168–174, 2011

Key words: crosslink; gels; benzophenone; photochemistry; swelling

INTRODUCTION

The physical properties of polymer solutions can be modified by crosslinking the chains to form an extended network (Fig. 1). Such networks offer increased durability[1] compared to their uncrosslinked counter-parts and are pertinent in a variety of current and future applications including absorbent[2,3] and elastic[4] materials, photoresists for micro- and nanofabrication,[5,6] membranes,[7,8] tissue engineering,[9] and controlled drug release.[10] The properties of crosslinked polymers depend on the crosslink density. As more crosslinks are formed the viscosity of the sample will increase. At the gel point the system undergoes a sharp transition at which the network becomes macroscopic and acts like an elastic solid rather than a viscous liquid.[11] Such a network is said to be infinite with every chain forming a bond with at least two other chains. When such a gel is placed in a good solvent, rather than dissolve, the gel will absorb the liquid and swell. Although a gel has mechanical properties associated with solids such as a nonzero sheer modulus, a large fraction of the gel can consist of solvent.[12] Some gels can absorb an amount of solvent that is hundreds of times the mass of the dry gel.[2,3]

A variety of photochemical methods have been reported for crosslinking polymers.[6] Many methods rely on crosslinkable pendant groups in the chain. Polymers containing groups susceptible to polymerization via a photo-initiated process provide suitable pendant groups for photo-crosslinking. For example, acetylene containing polymers have been crosslinked by irradiation in the presence of tungsten hexacarbonyl.[13] Other methods require only a photo-active functional group. Polymers containing various C=C groups can be dimerized via a photo-induced cycloaddition. Specific examples include polymers containing pendant cinnamate[14] and anthracene[15,16] groups. Irradiation of polymers containing phenolic O—H groups results in the cleavage of the O—H bond.[17] The resulting phenoxyl radicals can dimerize to form a crosslink. The reaction is facilitated in the presence of oxygen, which can abstract a hydrogen atom from the phenolic O—H group. Poly (styrene) (PS) similarly undergoes crosslinking by direct excitation of the phenyl ring.[18,19] Energy transfer results in the cleavage of a benzylic C—H bond. The resulting radicals undergo secondary processes that result in crosslinks. Polymers containing photo-active pendant groups that can generate species that react with C—H and other common functionalities upon absorption of a photon have also been used to crosslink polymers. Pendant benzophenone[20] and azide[21]
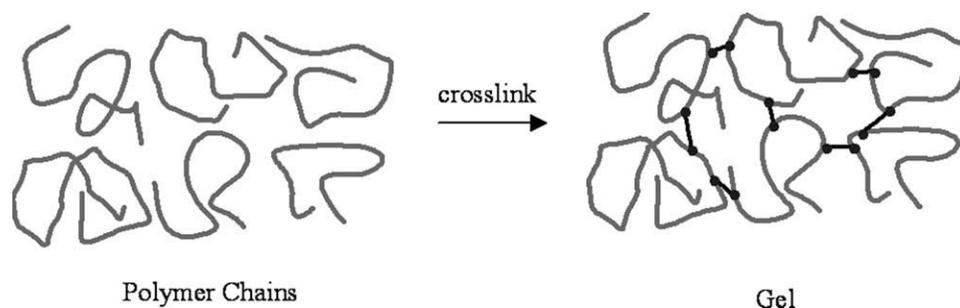
Figure 1 Schematic of the transformation of a group of polymer chains (left) into a single gel of crosslinked macromolecules (right).

moieties have been used to effect crosslinks in this way. Incorporating chromophores that react with C—H and other functionalities into bifunctional molecules provides a more general protocol for crosslinking, allowing networks to be formed from pre-existing polymers that do not contain photo-active groups.[22,23] Crosslinks are generated by recombination of macroradicals or recombination of both sides of the bi-functional molecule with a polymer. Monofunctional reactive compounds that can abstract only one hydrogen atom to form radicals are also capable of generating crosslinks in polymers by forming macroradicals that recombine to form covalent bonds.[24,25] Even more general, irradiating polymers with deep UV can cause crosslinking by chain scission followed by recombination of the resulting radicals.[6] This can potentially damage functional groups in the chain, compromising the functional properties of the resulting crosslinked network.

The ability to crosslink polymers without prior chemical derivatization or synthesis of a polymer with pendant photo-active groups is of interest because it avoids the often-laborious and expensive task of synthetic chemistry. We previously demonstrated a photochemical method for crosslinking and patterning pre-existing poly (styrene) (PS) films through the use of bisbenzophenone additives.[23] In this report we utilize the methodology for crosslinking polymers in solution to form macroscopic networks. We provide evidence that crosslinking results from the photo-generation of radical species. We compare the swelling properties of networks formed by both *bis*- and *mono*-functional benzophenone.

METHODS

bis-**BP** was synthesized according to a previously reported procedure.[23] After chromatography the product was further purified by recystallization from methanol.

Photochemical crosslinking in solution

Both PBD and PEO gels were prepared in solutions that were deoxygenated by bubbling with argon for 10 min followed by irradiation with a Rayonet photochemical reactor containing bulbs that emit at 350 nm. In a typical procedure for preparing PBD gels 3.5 μmol (0.01744 g) of *bis*-**BP** were added to a solution of 27.4 μmol (0.01312 g) of PBD in 2 mL of benzene. The sample was irradiated for 2 h. In a typical procedure for preparing PEO gels 29.2 μmol (0.01397 g) of *bis*-**BP** was added to a solution of 0.097 μmol (0.0194 g) of PEO (200,000 K) (Acros) in 2 mL of acetonitrile. PEO gels made with **BP** (Acros) were similarly prepared using a 2× molar amount of **BP** to keep the amount of chromophores equal between the two samples. Samples were irradiated for 5 h and 40 min.

Swelling measurements

Photo-generated gels were soaked in good solvent for 3 days, changing the solvent each day before performing swelling measurements. Gels were then dried at room temperature in a vacuum oven until an unchanging dry weight was obtained. Gels were then soaked in a given solvent for 1 day. Gels were removed from the solvent, lightly tapped with Teflon tape to remove excess solvent at the surface and weighed. Gels were then placed back in the vacuum oven to repeat the measurements.

Instrumental measurements

EPR measurements were performed using a Bruker EMX EPR spectrometer. Photo-generated PEO gels (∼ 4 h of irradiation with set-up described above) were soaked overnight in a solution of 33.4 μmol (0.00568 g) of 4-Oxo-Tempo in 6.7 mL of acetonitrile. The nitroxide solution was removed, the samples were each rinsed twice with DI water, and EPR spectra were taken of the two gels.

RESULTS AND DISCUSSION

Benzophenone chromophores[26] are known to undergo hydrogen abstraction reactions with hydrogen atom donors such as C—H groups, and thus are
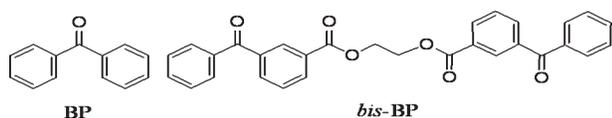
Figure 2 Structure of photo-active crosslinkers.

capable of crosslinking a wide variety of different polymer types as long as they possess C—H bonds. We examined the solution-phase crosslinking potential of both *bis*- (*bis*-**BP**) and *mono*-functional benzophenone (**BP**), both of which are shown in Figure 2. Benzophenone is well suited for our studies for a variety of reasons. It is generally not reactive when kept in the dark. It can be excited at wavelengths above 350 nm, which is generally less destructive than shorter wavelength UV. Its photophysical and photochemical properties have been well studied, including its propensity for hydrogen abstraction.[26]

BP has previously been shown to crosslink polymers.[24] The proposed mechanism involves the formation of macroradicals by hydrogen abstraction followed by recombination. We reasoned that incorporating multiple benzophenone chromophores into one molecule should increase the chances for crosslinking a variety of polymer types with different C—H bond strengths and in different environments

because this allows for more than one plausible mechanism for crosslinks to form as shown in Figure 3. Irradiation is expected to produce an excited n–π* state that intersystem crosses to the triplet.[26] One of several deactivation pathways includes hydrogen abstraction of a nearby C—H group on a polymer chain. Hydrogen abstraction will form radicals that can recombine to form covalent bonds. Two potential recombination pathways can result in crosslinks. First, radical centers on the polymer chains can recombine with each other. This requires that the photo-generated macroradicals are located sufficiently close to each other. Note that this pathway may be limited in environments where chain motion is hindered. Second, the inclusion of two benzophenone chromophores supplies an additional crosslinking pathway that circumvents the need to have two macroradical centers in close proximity. Recombination of two benzophenone ketyl radicals at the ends of a single molecule of *bis*-**BP** with macroradicals results in crosslinks without the need for two interacting polymer radicals. The main possible side reactions include recombination of the ketyl radicals to produce pinnacol derivatives that may or may not act as extended crosslink bridges and disproportionation products.
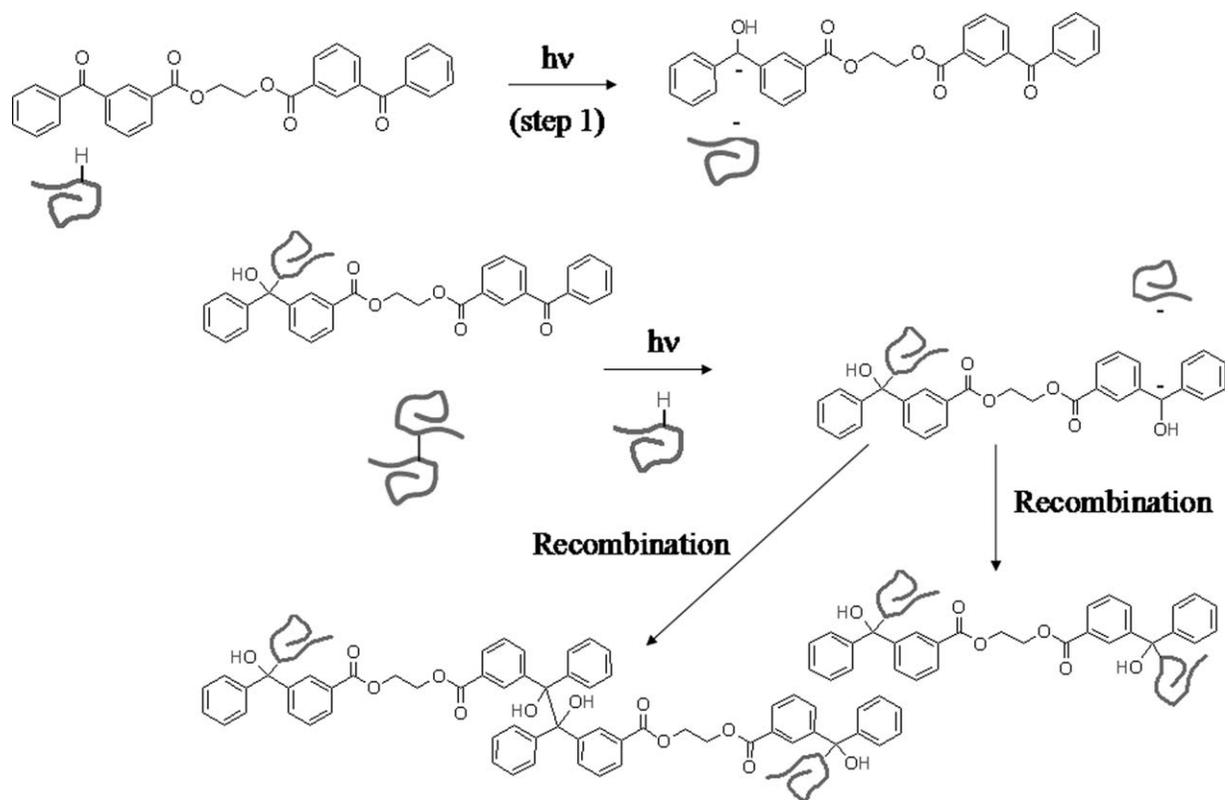

Figure 3 Two pathways are proposed for crosslinking of polymers by bis-BP. In the first, radicals created on polymer chains by hydrogen abstraction can recombine to form crosslinks. In the second, after bis-BP abstracts hydrogen atoms from polymer chains, recombination between a polymer radical and a benzophenone ketyl radical result in a covalent bond. When this happens on both benzophenone chromophores, a crosslink will result.
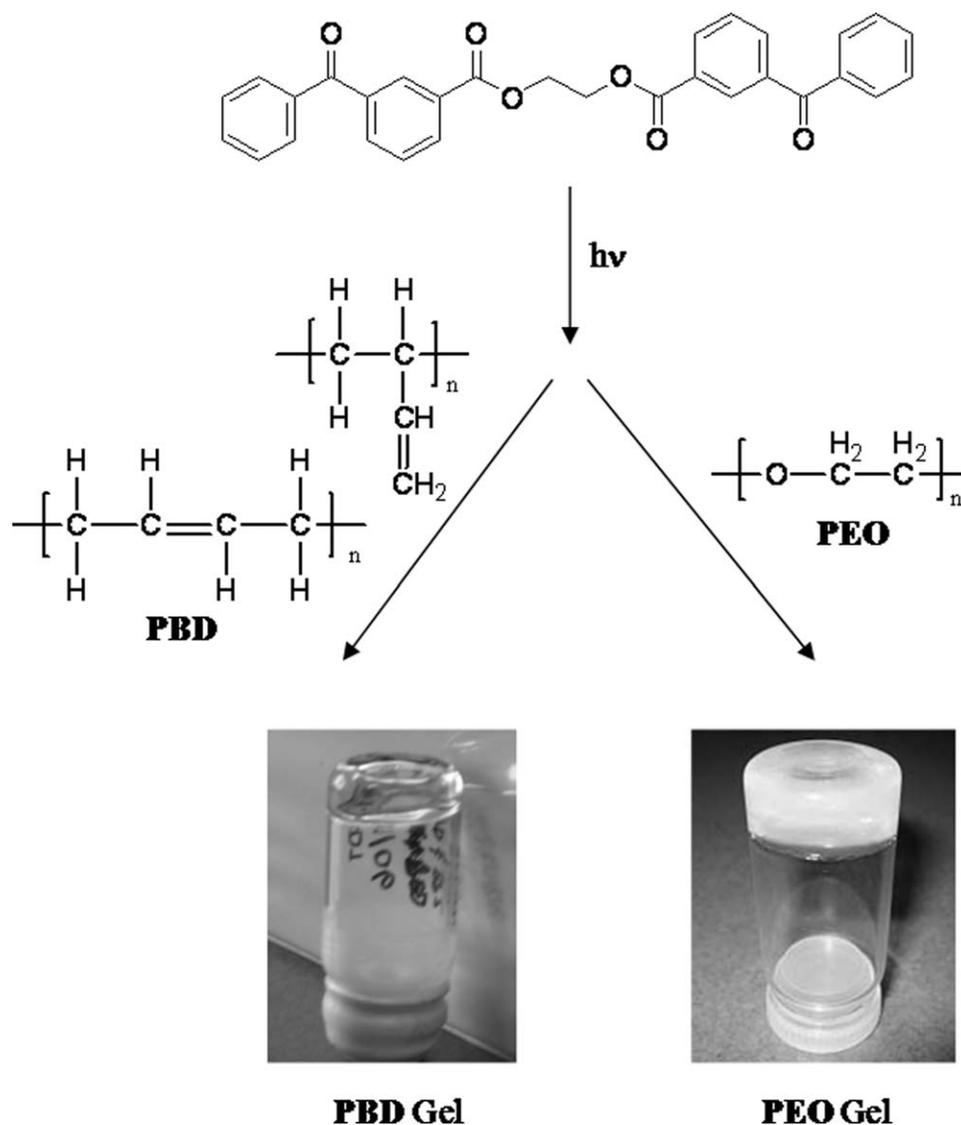
Figure 4 Photo-generated PBD and PEO gels using bis-BP. Gels were also obtained when BP was used as the crosslinker.

To test the versatility of the photo-crosslinking reaction in solution we selected poly (butadiene) (PBD) and poly (ethylene oxide) (PEO), two polymers containing different physical and chemical properties. For example, PEO is hydrophilic and expected to result in a hydrogel when crosslinked, whereas, PBD is hydrophobic and is not expected to absorb an appreciable amount of water. Regardless of the physical and chemical properties, irradiation of both polymers in the presence of **BP** or bis-**BP** resulted in the precipitation of insoluble material from deoxygenated solutions. Gels photogenerated from bis-**BP** are displayed in Figure 4. Irradiation of deoxygenated polymer solutions without crosslinker did not result in the formation of gels.

A variety of methods have been used to characterize crosslinked networks including small angle neutron scattering,[27] pulsed-field gradient,[28,29] and solid-state NMR,[30,31] IR,[32] AFM,[33,34] and rheology[35] measurements. Swelling measurements provide a convenient technique for characterizing crosslinks in a variety of polymers that allows for the crosslink density to be calculated based on the ratio of the volume of the swollen gel to the dry gel.[11,36,37] We compared the crosslink density of PEO gels photogenerated using **BP** and bis-**BP** by analyzing the swelling ratios of the two gels using both toluene and acetonitrile as swelling solvents. These solvents were selected because their solubility parameters, 18.2 and 24.3 $(MPa)^{1/2}$, are slightly above and below that of PEO, 20.2 ± 2 $(MPa)^{1/2}$.[38] In addition, the volatility of these solvents was low enough such that a stable weight of swollen gel could be obtained. The PEO gels clearly swell in comparison with the dry gel as shown in Figure 5. From the swelling
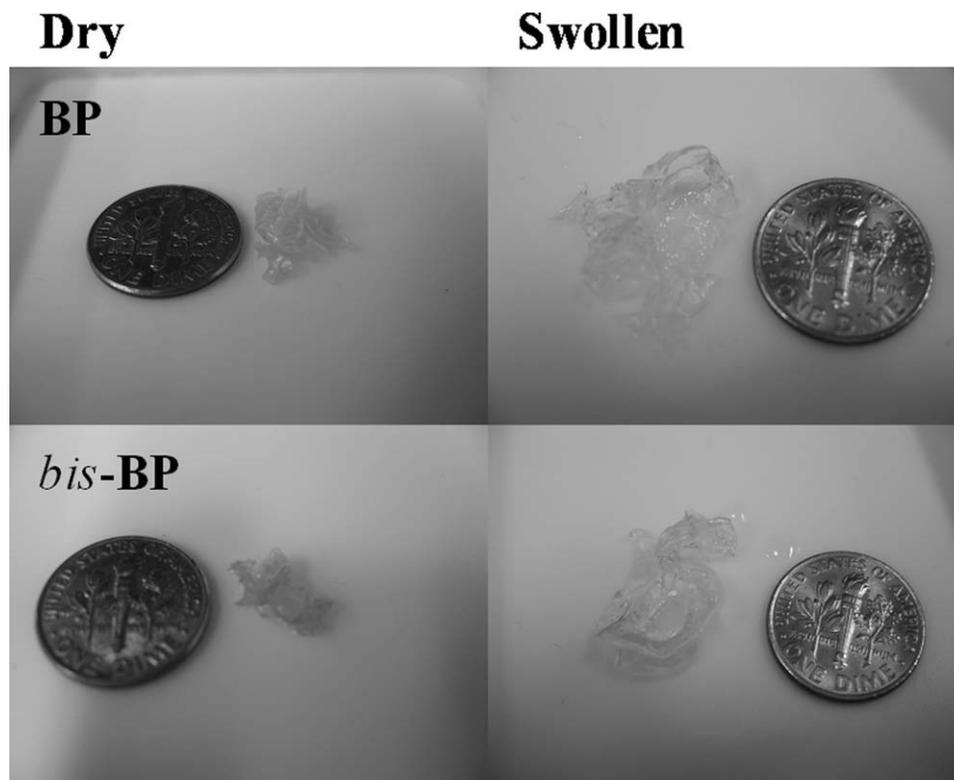
Figure 5 Dry and swollen PEO gels photo-generated by irradiation of acetonitrile solutions containing PEO and BP or bis-BP. Gels were soaked in acetonitrile for 12 h. Similar results were obtained using toluene.

ratio the molecular weight between crosslinks, M_c, can be calculated from the following equation:

$$1/(\nu M_c) = (\ln(1 - \nu_2) + \nu_2 + \chi_1 \nu_2^2)/(\phi(\nu_2^{1/3} - \nu_2/2)) \quad (1)$$

where ν is the specific volume of the polymer, ν_2 is the volume fraction of polymer, χ is the Flory interaction parameter and ϕ is the molar volume of solvent. ν_2 can be calculated from the swelling ratio, q, according to eq. (2):

$$q = V/V_o = 1/\nu_2 \quad (2)$$

where V is the volume of the wet gel and V_o is the volume of the dry gel. M_c values and the crosslink density, ν_x, for **BP** and bis-**BP** PEO gels are shown in Table I. The crosslink density was calculated from eq. (3):

$$\nu_x = 1/(\nu M_c) \quad (3)$$

A higher crosslink density was calculated for the bis-**BP** PEO gels regardless of the swelling solvent. We conclude therefore that the bis-**BP** gel is more heavily crosslinked than the **BP** gel. This is expected since bis-**BP** has more than one mode of forming crosslinks. When a **BP** ketyl radical recombines with a

polymer radical, a potential polymer–polymer crosslink is lost. However, when a bis-**BP** ketyl radical recombines with a polymer radical a polymer–polymer crosslink can still be formed if the second chromophore recombines either with a polymer radical or another bis-**BP** ketyl radical attached to a polymer.

We also examined the crosslink density using EPR spectroscopy. The line shape of an EPR spectrum relates to the rotational correlation time of the paramagnetic species.[39] Hindered molecules rotate more slowly, making it more difficult to align its magnetic moment with the applied magnetic field. Such a spectrum will typically have unequal peak heights and broaden in comparison to a sample in an environment where rotation is less hindered. Nitroxide molecules are common EPR probes because they contain stable radicals. We reasoned that if the

TABLE I
Comparison of the Molecular Weight Between Crosslinks (M_c) and Cross-Link Density (ν_x) for PEO Gels Photo-Crosslinked by BP and bis-BP

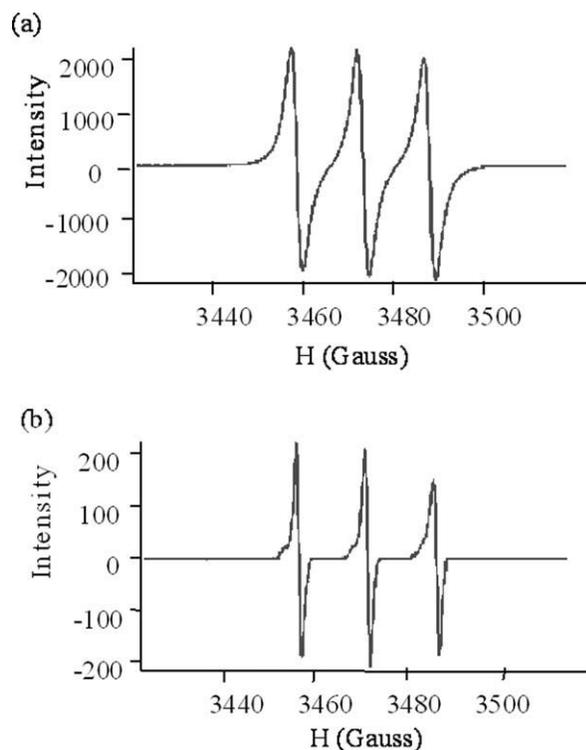| Crosslinker	Acetonitrile		Toluene	
	M_c	ν_x	M_c	ν_x
BP	8900 ± 1500	150 ± 20	7000 ± 4000	220 ± 90
bis-BP	3600 ± 800	380 ± 80	1300 ± 200	1000 ± 150

Figure 6 EPR spectra of 4-oxo-tempo in photo-generated gels from (a) BP and (b) bis-BP.

bis-**BP** gels are more heavily crosslinked than the **BP** gel, nitroxides absorbed into the gel should give a signal indicative of slower rotation. We incubated **BP** and *bis*-**BP** PEO gels overnight in acetonitrile solutions containing 4-Oxo-Tempo. After removing the nitroxide supernatant we took EPR spectra of the gels (Fig. 6). Each gel showed the characteristic three line EPR spectrum exhibited by nitroxide radicals, indicating that nitroxide absorbed into the gel. The gel photo-generated from **BP** [Fig. 6(a)] shows a much more intense signal, indicating that nitroxide more easily penetrated this gel. The spectrum of the gel photo-generated from *bis*-**BP** [Fig. 6(b)] shows an attenuated signal for the peak at the highest field, which is a sign of a longer rotational correlation time. The peaks for the **BP** gel are broader; however this can be a result of oxygen penetrating the network. We attribute these results to a higher crosslink density in the *bis*-**BP** gels since a higher crosslink density is expected to make the gel less permeable and to inhibit the rotational diffusion of molecules that are absorbed into the gel. In conjunction with the swelling studies described above, we conclude that *bis*-**BP** is a more efficient crosslinker than **BP**.

CONCLUSIONS

We have shown that both **BP** and *bis*-**BP** are capable of crosslinking polymers in solution. In comparison with **BP**, analysis of the swelling ratios of photo-generated PEO gels as well as EPR measurements of absorbed nitroxide probes shows that *bis*-**BP** gels are more highly crosslinked. Although we have focused on crosslinking traditional macromolecules, we expect that the methodology is suitable for stabilizing and networking a variety of systems including emerging materials based on self-assembly and supramolecular chemistry.[40,41]

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