Photorheology of UV-crosslinkable polymer solutions

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ABSTRACT

Anthracene moieties are known to undergo photo-induced cycloaddition under ultraviolet (UV) illumination and can therefore be utilized in preparing photo-dynamic materials. In this study, we investigate the viscoelastic properties of anthracene-containing random and triblock copolymer solutions during in-situ UV irradiation. Among other findings, we observe that the crosslinking of the anthracene-containing polymer solutions can also take place in dark.

INTRODUCTION

A wide variety of application from coating and glues to biomedical materials exist for covalently crosslinked materials. However, the robustness of their structure makes them hard to remove or reprocess. Reversibility of the covalent crosslinks would not only allow for convenient processing but also for easy removal and recycling.[1]

ABA triblock copolymers are attractive candidates for gels and crosslinked materials, due to their self-assembling tendencies.[2–5] The mechanical properties of ABA triblock copolymer gels can be tuned by the polymer concentration, but also by the nature and length of the midblock.[6] Therefore, controlled polymerization techniques are opening the way to engineer and control the nanoscale architecture of polymer assemblies.[4,7] Self assembled gels from ABA triblock copolymers rely on transient physical crosslinks, which are susceptible to creep flow over time. Therefore, introducing chemical crosslinks within the physical crosslinks improves the mechanical stability of the gels.[3]

Light is an attractive tool to controlling both the formation and dissociation of self-assembled structures. Light offers high-resolution, temporal and spatial control, and repeatability to the crosslinking process. In addition with light, there is no need for physical contact with the material, which could introduce contaminants into the system.[8–10]

Photodimerization of anthracenes has been used from crosslinking[11] and end-to-end coupling[12,13] of polymers to optical switches.[14] This reversible photodimerization occurs under the irradiation of the material with UV-light (230-365 nm). Although the photodimerization process is fast, it is temperature dependent and that fluorescence, internal conversion, and intersystem crossing compete with the photodimerization process.[15,16] The dimers can be broken by either by heat or irradiation with UV-light (250-290 nm), however, irradiation also causes the anthracenes to photodimerize.[16] Softer UV-light or visible light can also be utilized in the photodimerization and dissociation, however the irradiation times can be up to 48 hours.[17] The thermal dissociation kinetics and dissociation

temperature of the dimers is dependent on the structure of the anthracene derivative. In solutions, the dissociation times of small molecular anthracene derivatives can vary from minutes to days at room temperature.[16]

EXPERIMENTAL

Polymer synthesis

Poly(anthracen-9-ylmethyl methacrylate-co-lauryl methacrylate), P(AMM-LMA): Anthracen-9-ylmethyl methacrylate (AMM, 1.03 g, 3.6 mmol), lauryl methacrylate (LMA, 0.26 g, 1.02 mmol), 4,4′-Azobis(4-cyanovaleric acid) (18.9 mg, 0.067 mmol), and azoisobutyronitrile (5.60 mg, 0.34 mmol) were dissolved in cyclohexanone (4 mL) under a nitrogen atmosphere, and heated to 90 °C for 23 hours. 1.08 g of polymer was obtained by precipitation in methanol (M_n = 20 200 g/mol, PDI = 1.13). The polymer contains 71 % anthracene methacrylate, which was determined by ^{1}H-NMR.

Poly(lauryl methacrylate), P(LMA): LMA (3.47 g, 13.7 mmol) was polymerized in cyclohexanone (4 mL) with ethane-1,2-diyl bis(2-bromo-2-methylpropanoate) (30.9 mg, 0.85 mmol), CuBr (25.4 mg, 0.18 mmol), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 27.9 mg, 0.19 mmol) under a nitrogen atmosphere for 2.5 hours at 60 °C. 2.1 g of polymer was obtained by precipitation in acetone (M_n = 41 000 g/mol, PDI = 1.09).

Triblock copolymer, P(AMM-LMA)-P(LMA)- P(AMM-LMA): A mixture of LMA (0.50 g, 1.98 mmol), and AMM (0.25 g, 0.89 mmol) was polymerized in cyclohexanone (4 mL) with poly(lauryl methacrylate) (0.37 g, 0.009 mmol), CuCl (13.0 mg, 0.13 mmol), and HMTETA (27.9 mg, 0.19 mmol) under a nitrogen atmosphere for 18 hours at 60 °C. 270 mg of polymer was obtained by precipitation in methanol (M_n = 52 900 g/mol, PDI = 1.28). The polymer contained 21 % anthracene methacrylate, which was determined by ^{1}H-NMR.

Rheological characterization

Samples for rheological characterization were prepared by dissolving the copolymers in toluene at various weight concentrations (*c* = 0.3-10 wt%). Rheological measurements were performed using a stress-controlled Anton Paar Physica MCR 301 rheometer equipped with a 25-mm diameter parallel plate geometry. A transparent lower plate was used to illuminate the sample from underneath with an Omnicure S1500 Spot UV Curing System. This light source was used in combination with a bandpass filter glass (FGUV5, Thorlabs) to provide UV-light with a peak wavelength of 365 nm and irradiance of 40 mW/cm^2. A small measurement gap of 0.1 mm was used to ensure homogeneous illumination of the sample. Time sweep measurements (f = 1 Hz, γ_0 = 0.1 %) were carried out to study the crosslinking of the anthracene polymer solutions under three different illumination conditions: upon continuous UV-irradiation, under periodic UV-irradiation, and in dark. Following the time sweep measurements, frequency sweep (f = 0.1-10 Hz, γ_0 = 0.1 %) and strain sweep (f = 1 Hz, γ_0 = 0.001-10 %) measurements were performed on crosslinked samples. All measurements were performed at 22 °C with the temperature being controlled by a Peltier hood. This hood also shielded the sample from ambient light. An evaporation blocker was used to prevent the evaporation of the solvent over the course of the measurements.[18]

RESULTS AND DISCUSSION

Random and triblock copolymers of lauryl methacrylate (LMA) and anthracen-9-yl methyl methacrylate (AMM) were prepared by reversible addition−fragmentation chain-transfer polymerization (RAFT) and atom transfer radical polymerization (ATRP), respectively. The triblock copolymer had a middle segment of P(LMA) and two segments of P(AMM-co-LMA) on both ends (Fig. 1). The
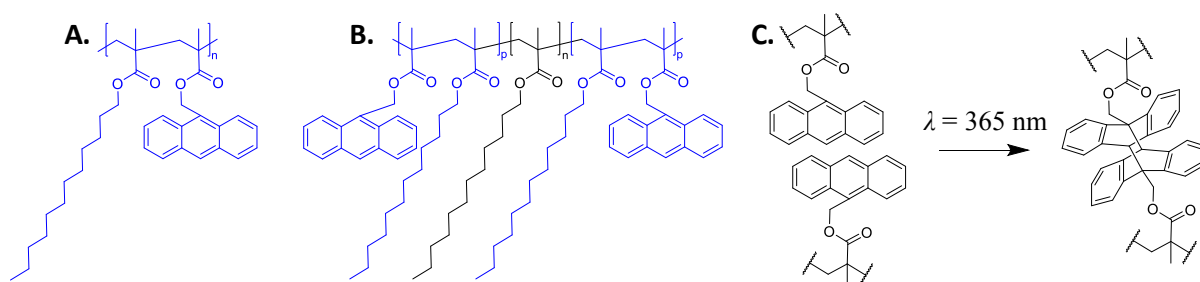
Figure 1. Structures of the random (A) and triblock copolymer (B), and the photocrosslinking of the anthracene units (C).

polymer composition was determined by ^{1}H-NMR: The random copolymer contained 71 mol-% AMM (M_n = 20.2 kg/mol, PDI = 1.13) and the block copolymer 21 mol-% AMM (M_n = 52.9 kg/mol, PDI = 1.28).

Fig. 2(a) shows the evolution of the storage modulus (G') and the loss modulus (G'') in P(AMM-LMA) random copolymer solutions under periodic UV-irradiation (λ = 365 nm). In this measurement, the light source was switched on and off every two minutes as illustrated by the bright and shaded areas in the graph. The UV-induced crosslinking of the anthracene groups results in the solidification of the P(AMM-LMA) solutions, as manifested by increasing G' and G''. Moreover, the crosslinked solutions are observed to be highly elastic as G' dominates

over G'' from the early stages of the crosslinking process. The crosslinking reaction and subsequent solidification occurs more slowly when the polymer concentration is decreased, and at the lowest polymer concentration of 0.3 wt% solidification does not take place at all as there are too few crosslinks to form a continuous polymer network. It is also worth noting that the crosslinked P(AMM-LMA) solution is stiffer the higher the polymer concentration. This is due to the increasing crosslinking density.

The irradiation of the P(AMM-LMA) solutions with UV-light also results in the development of negative normal forces in the rheometer. This is due to the shrinkage (densification) of the test specimen. As shown in Fig. 2(b), periodic UV-irradiation
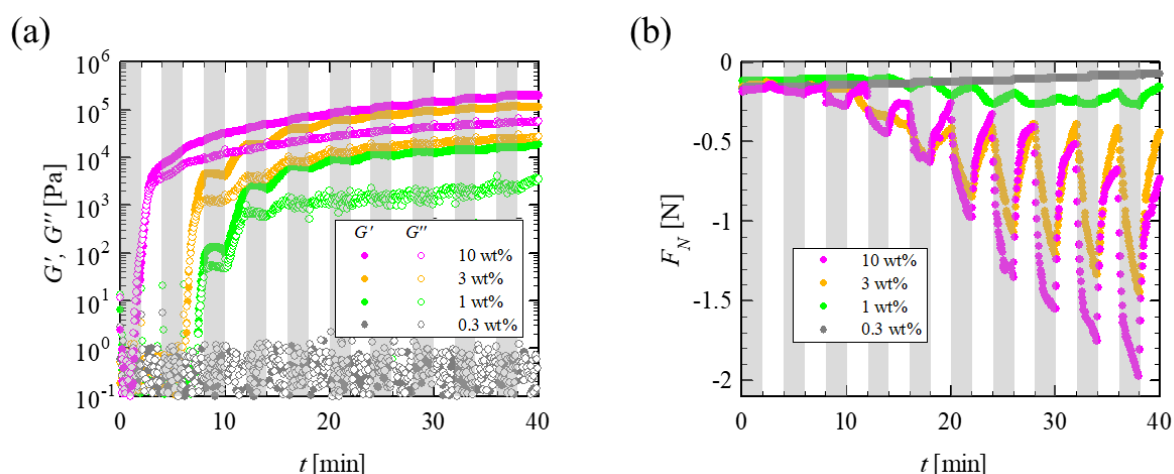

Figure 2. The evolution of (a) the storage and loss modulus and (b) normal force at various P(AMM-LMA) concentrations during periodic UV-irradiation. The bright and shaded areas in the graphs correspond to the periods when the UV-light was switched on and off, respectively.

of the P(AMM-LMA) solutions causes cyclic fluctuation of the normal force. The magnitude of the negative normal force changes sharply when the light source is switched on and off. However, the normal forces only develop when the solutions are sufficiently crosslinked (cf. the increase of *G'* and *G''* in Fig. 2(a)).

Interestingly, the pattern in the evolution of the viscoelastic properties changes during the repetitive illumination with the UV-light. This is illustrated in Fig. 3 where the evolution of *G'* during the latter part of the periodic UV-irradiation test is shown for 3 wt% P(AMM-LMA) random copolymer solution. Note that a linear scale is used on the y-axis to better visualize the effect of UV-illumination on the evolution of *G'*. It is evident that towards the end of the measurement, crosslinking occurs also during the periods when the UV-light is switched off. Correspondingly, *G'* is observed to decrease for some tens of seconds after the UV-light is switched on. Similar trends in the evolution of *G'* during periodic UV-irradiation were observed in the more concentrated 10 wt% P(AMM-LMA) solution.

To further investigate this phenomenon, the time evolution of the viscoelastic properties was measured while the sample was kept in dark (the UV-light source was switched off and the sample was protected from ambient light by the Peltier hood). The data for the 3 wt% P(AMM-LMA) random copolymer solution is shown in Fig. 4. The crosslinking of the polymer solution is observed to proceed even in dark conditions, albeit at a much lower rate than under periodic UV-irradiation. It is also worth noting that the plateau values for *G'* and *G''* are much lower for the sample crosslinked in dark than for the sample crosslinked with UV-light. This kind of "dark curing" has been previously observed in other types of photocrosslinkable polymeric systems.[19,20] We may speculate that, in our case, this phenomenon is caused by kinetic effects or the presence of a second crosslinking mechanism. However, further studies are needed to confirm the origin of our observations.
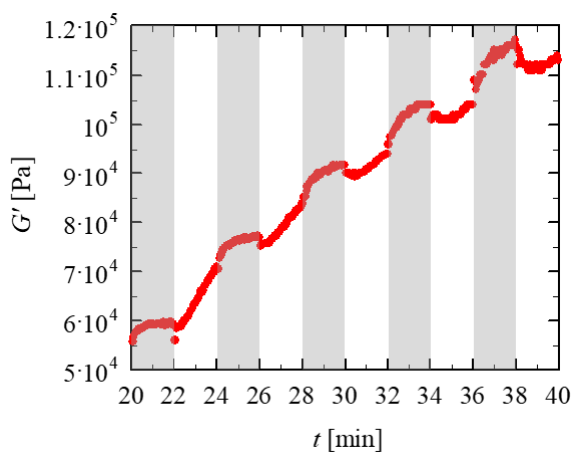

Figure 3. The evolution of the storage modulus during the latter part of the periodic UV-irradiation test for the 3 wt% P(AMM-LMA) random copolymer solution. The bright and shaded areas in the graphs correspond to the periods when the UV-light was switched on and off, respectively.
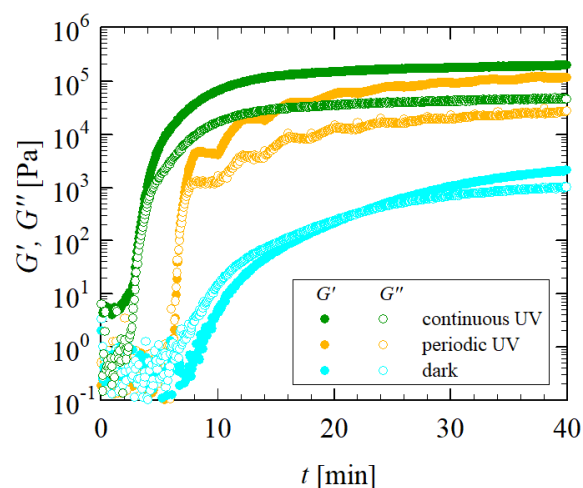

Figure 4. The evolution of the storage and loss modulus under different illumination conditions for the 3 wt% P(AMM-LMA) random copolymer solution.
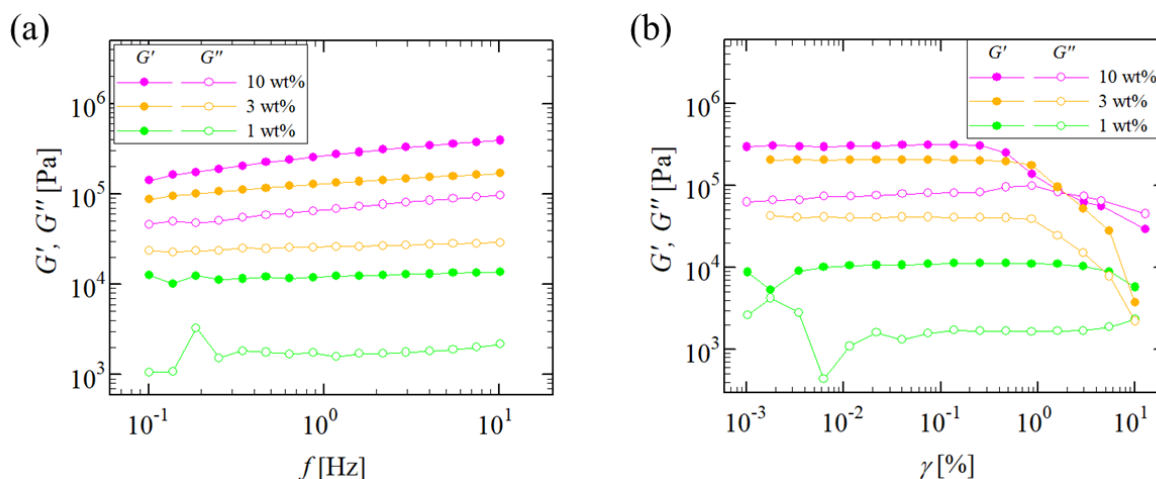
Figure 5. (a) The frequency sweep and (b) strain sweep results for crosslinked P(AMM-LMA) solutions of different polymer concentrations.

Fig. 5(a) shows the frequency sweep data for the crosslinked P(AMM-LMA) random copolymer solutions. G' and G'' are observed to be almost independent of the frequency, which is characteristic of chemical gels. As was discussed already in connection with Fig. 2(a), the increase in G' with increasing polymer concentration is indicative of increased crosslink density. The number of crosslinks per unit volume, v_e, can be estimated using the following equation:[21]

$$G' = v_e R T \qquad (1)$$

where R is the gas constant and T is the temperature. The crosslink density is estimated to vary from about 5 mol/m^3 (at 1 wt% polymer concentration) to about 58 mol/m^3 (at 10 wt% polymer concentration). Furthermore, Fig. 5(b) shows the strain sweep data for the crosslinked P(AMM-LMA) samples. As could be expected, the linear viscoelastic region extends to higher strain amplitudes in less crosslinked samples, i.e. at lower polymer concentrations.

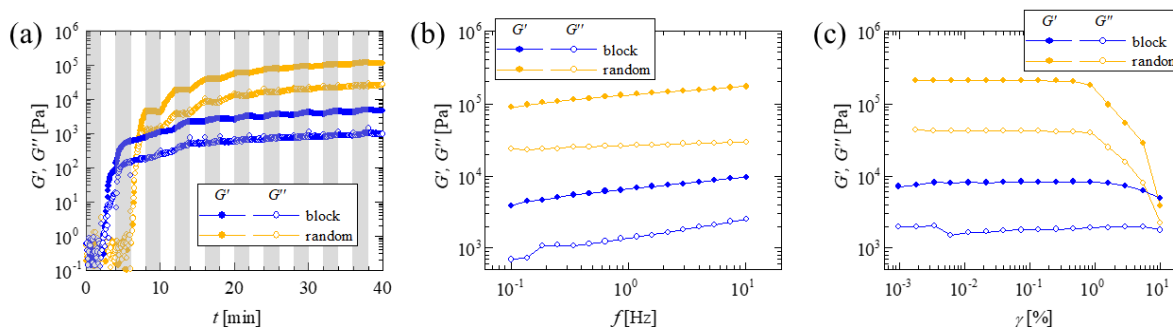To complete our study, we compare the rheological properties of the random and

Figure 6. Comparison of the rheological properties of the P(AMM-LMA)-P(LMA)-P(AMM-LMA) block copolymer solution and P(AMM-LMA) random copolymer solution at 3 wt% polymer concentration. Part (a) shows the evolution of the storage and loss modulus during periodic UV-irradiation (the bright and shaded areas correspond to the periods when the UV-light was switched on and off, respectively). Parts (b) and (c) show the frequency sweep and strain sweep data for the crosslinked samples, respectively.

block copolymer solutions (Fig. 6). The time sweep, frequency sweep and strain sweep data clearly demonstrate that the block copolymer solution is considerably softer than the random copolymer solution at an identical polymer concentration of 3 wt%. This is due to the block copolymer architecture consisting of a softer middle block and lower crosslink density (fewer anthracene units). Finally, the wider linear viscoelastic region and more gradual drop of *G'* and *G''* in the nonlinear viscoelastic region demonstrate the superior ductility of the crosslinked block copolymer solution over the crosslinked random copolymer solution (Fig. 6(c)).

CONCLUSION

In this work, we compare the photocontrollable rheological properties of solutions of random and ABA-type triblock copolymers consisting of anthracene and non-photoactive monomers. UV-illumination is observed to increase the extent of cycloaddition of two anthracene units, thus creating cross-linking. In addition to the UV-induced crosslinking, high polymer concentration (≥3 wt%) solutions are observed to undergo crosslinking in dark. This is possibly due to kinetic effects or the presence of a second crosslinking mechanism. As compared to random copolymer system, crosslinked triblock copolymer system, comprising a soft block in between of the photocrosslinkable blocks, provides superior ductility and thus being more suitable for applications such as stereolithography and flexible sensors.

ACKNOWLEDGMENTS

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