Photocross-linking Kinetics Study of Benzophenone Containing Zwitterionic Copolymers

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ABSTRACT: The kinetics of benzophenone (BP) and its derivatives have been widely studied in different solvents by nanosecond laser flash photolysis as well as in the polymer matrix. With the development of functional polymer coating, BP, as well as other photocross-linkers, has been incorporated into the polymer backbone or side chain to form the covalent connection between polymer coatings and substrates, which can improve the mechanical and chemical stability of the coatings. In this work, a series of BP pendant zwitterionic copolymer kinetics were investigated using UV–vis for the first time. Because of the high hydrophilicity of the zwitterionic monomer, the influence of the polymer matrix’s polarity on the cross-linking rate was observed. With a higher zwitterionic percentage in the copolymer, the polarity of the copolymer increases, BP reactivity decreases, and a hypothesis between the BP rate constant and partial coefficient log P was raised. Moreover, the thermal property is also an important factor affecting the BP reactivity. For polymers with high glass-transition temperature, the reactivity was not dominated by the chemical environment such as polarity, and the restricted segment movement reduces the cross-linking rate. Additionally, the ring substituents show similar effects to BP pendant copolymers as with small molecules. Electron-withdrawing groups help to stabilize the BP triplet radical and facilitate cross-linking, while electron-donating groups work conversely. Therefore, polarity, thermal properties, and substituents should be taken into consideration when designing BP-containing functional polymers.

INTRODUCTION

Photochemical methods are some of the most versatile techniques for both synthetic and natural polymer modification. Many photoreactive reagents have been used to functionalized surfaces for different applications, including diazirines, aryl azides,1,2 nitrobenzils,3,4 cyclic disulfides,5,6 and benzophenone (BP).7 BP and its derivatives are perhaps the hydrogens with extremely high reactivity. However, the represented as a diradical, is well known to abstract aliphatic excited to a singlet state (S\text{1}) that rapidly and efficiently undergoes inter-system crossing to yield the lowest energy triplet. The n−π* triplet (T\text{1}), which can be represented as a diradical, is well known to abstract aliphatic hydrogens with extremely high reactivity. However, the π−π* charge transfer (CT) is much less reactive than n−π*. Any change in the energy level of n−π* and π−π* would affect the cross-linking speed.15

The kinetics of BP derivatives have been well studied in various conditions. The hydrogen abstraction of BP triplet was investigated using nanosecond flash photolysis measurements and activation energy in different solvent systems, including ethanol, isopropanol, and cyclohexane.16,17 The reactivity of BP is affected by the solvent condition, as the solvent polarity will influence the relative energy levels of BP derivatives, even inverting the CT and n−π* states when they are close in energy levels. Generally, the excited state energy will decrease in the polar solvent if its polarity is higher than that of the ground state. Increasing the solvent polarity can shift the n−π* triplet to the π−π* or CT state, which prevents reactions of some BP derivatives in a polar solvent. However, even when the lowest energy triplet is the π−π* or CT state, some extent of reactivity will be observed as thermal (vibrational) fluctuation to the n−π* triplet.18−21 The relationship between the spectroscopic and photochemical properties have also been studied in detail in substituted BPs. Electron donors increase the electron density at the carbonyl, making it less electrophilic
and therefore less reactive, inhibiting H-abstraction. Electron-withdrawing groups on BPs have an opposite effect, increasing the reactivity of the n−π* radical.18,22,23 Other factors that affect the kinetics of BP include stereoelectronic control, regioselectivity, and heterologous behavior.15,24,25

As BP is widely used in the polymer modification, the reactivity and kinetics of BP in the polymer matrix also attracted lots of attention. Reactions in polymer solids greatly differ from those in solution mainly because the mobility of the reactants is far more suppressed in the former than in the later.26–28 Another important difference is that reactions in polymer solids frequently proceed in a heterogeneous fashion, owing to the aggregation or the free volume distribution.26,28,29 In the case of BP and its derivatives, the quantum yield in solid films above glass transition temperature (Tg) is the same as that in solution, but it follows other mechanisms when below Tg.30,31 Other factors that influence reactions in polymer solids also include chain scission, excited energy transfer, and migration and electron transfer.32 BP kinetics in poly(methyl methacrylate), poly(isopropyl methacrylate), and poly(methyl acrylate) was studied at different temperatures. The decay of BP triplet in all three polymers followed an exponential trend for the temperature range T > Tg and nonexponential trend for the temperature range T < Tg which is controlled by both diffusion and chemical steps.33

Polarity is a complex factor and encompasses the range of noncovalent interactions, including dipolarity/polarizability and hydrogen bonding. The polymer polarity depends on the polarity of the monomers, polymer composition, conformation, and configurations.34 Contact angle measurements were generally used for the investigation of surface polarity (hydrophilic–hydrophobic properties), and the polarity of the polymer microenvironment can be estimated by the polymer solubility in a binary solvent.35 Herein, partition coefficients, P, are used to estimate the polymer polarity. P is a measurement of the different solubility of the compound in two immiscible solvents and provides a useful quantitative parameter for representing the lipophilic/hydrophilic nature of the substance.36,37 The most commonly used solvent system is octanol/water (eq 1). A negative value of log P means the compound has a higher affinity for the aqueous phase, and a positive value of log P indicates the compound is more lipophilic. The log P value is generally not difficult to determine experimentally, but it can also easily be estimated using the methodology as a sum of fragment-based contributions and correction factors. The method is very robust and is able to process practically organic and most of the organometallic molecules.38 log P can be used in quantitative structure–activity relationship studies and rational drug design as a measure of molecular hydrophobicity and has become a key parameter in studies of the environmental fate of chemicals.39

\[
P = \frac{[\text{compound}]_{\text{octanol}}}{[\text{compound}]_{\text{water}}} \tag{1}
\]

The BP kinetics studies mentioned previously have focused on small molecules, either in solution or a polymer matrix.12,16,33,39 Recently, the development of BP in the polymer community has focused on BP pendant copolymers, which provide more straightforward synthesis and applications. Antifogging,40 antimicrobial,41 anti-icing,42 and antifouling43 surfaces all have been synthesized and stabilized using BP as a monomer component. More functional polymers can be covalently attached to alkyl substrates by incorporation of BP components. However, the kinetics of BP pendant polymer has not yet been investigated in-depth.

Zwitterionic polymer coatings have attracted tremendous attention because of their ultra-low fouling properties, but the coating stability was under challenging because of its high solubility. To permanently attach zwitterionic polymers thin films to a substrate, photochemistry was considered to be a universally effective method.44 Among these zwitterionic polymers, 2-methacryloyloxyethyl phosphorylcholine (MPC) polymers are advantageous because of their simple molecular design and synthesis process. Additionally, recent studies reported by Ishihara et al. demonstrated the importance of the photochemistry of MPC-coated materials in the application of medical devices.44–46

The kinetics of BP as a monomer moiety in the MPC copolymers was investigated in this study. The ratio of polymer components demonstrated significant influence on the rate of BP cross-linking. We hypothesized that the polarity of the polymer matrix would affect the triplet energy level and the reactivity of the BP pendant groups, just as the polarity of solvent systems to BP derivatives. A series of copolymers with different hydrophilicity were synthesized by radical polymerization, and the polarity of each polymer has been evaluated by the partition coefficient, log P. A linear relationship between log P and rate constant of BP was observed for zwitterionic polymers with Tg lower than irradiation temperature, and its application range was described. Additionally, BP with different substituents was also incorporated into the polymer chain, and the kinetics was also investigated using UV–vis.

## RESULTS AND DISCUSSION

The zwitterionic polymers (BPMPC37, BPMPC55, BPMPC73, and BPMPC91, Table 1) were synthesized by radical polymerization (Scheme 1), and the polymer composition was confirmed using 1H NMR spectroscopy (Figure S3). The kinetics of the BP copolymer was complicated and can be influenced by many factors, including the mole ratio of BP. Therefore, the percentage of the BP component was fixed in this study, and the ratio of other components was adjusted.47 The monomer unit composition was confirmed based on the following analysis: 3.25 ppm (−N(CH3)3, 9H) for MPC unit, 1.45−1.63 ppm (−CH2−, 4H) for the n-butyl methacrylate (BMA) unit, and 6.80−7.85 ppm (BP-H, 9H) for the BP unit. The monomer units in the polymer chain were randomly distributed, with a total composition approximately equal to that of the monomer feeding ratio (Table 1).

BPMPC kinetics calculation was based on the intensity of the carbonyl group in the UV–vis spectra. In the context of

| Table 1. Synthetic Results of BPMPC Polymers |
|-----------------------------------------------|
| composition (mol/%) in feed MPC/BMA/BP | initiator (mmol/mL) | composition (mol/%) in copolymer MPC/BMA/BP | yield (%) |
|-----------------------------------------------|
| BPMPC37 | 28.5/66.7/4.8 | 0.02 | 27.1/70.6/2.2 | 88.7 |
| BPMPC55 | 47.6/47.6/4.8 | 0.02 | 48.9/48.6/2.5 | 82.4 |
| BPMPC73 | 66.7/28.5/4.8 | 0.02 | 66.7/30.7/2.6 | 75.6 |
| BPMPC91 | 85.7/9.5/4.8 | 0.02 | 76.9/20.0/3 | 79.1 |
hydrogen abstraction, the carbonyl group of BP converts to the hydroxide group, and the intensity of the absorption peak decrease accordingly. Figure S6 shows the UV−vis spectra of BPMPC37, BPMPC55, BPMPC73, and BPMPC91, where the decreasing absorbance of the BP group at 255 nm occurred with increased irradiation time. For BPMPC37, the absorbance peak completely disappeared in less than 1 min; while for BPMPC91, the absorbance intensity maintained a small amount even after 10 min irradiation. The decrease of the cross-linking rate with the increase of the MPC percentage in the copolymer can be observed from the UV−vis spectra. The significant difference in the BP reactivity caught our attention.

To further understand the kinetics difference among all polymers, the conversion of crosslinking reactions was shown by plotting the decay of absorbance of the BP moiety as a function of irradiation time (Figure 1). As shown in Figure 1, with the increase of MPC percentage in the copolymer, the reactivity of BP cross-linking decreases. According to the previous studies, the triplet decay and hydrogen abstraction of BP derivatives in the polymer are affected by temperature and molecular motion of the matrix, free volume distribution (diffusion), and size and shape of the reaction groups.30,31 Different from the small molecule, BP pendent group is a side chain which hardly diffuses through the polymer matrix during the reaction. Additionally, the size and shape of the reactive groups are the same under this scenario. Herein, the thermal properties of the BPMPC polymer are investigated.

The thermal properties of BPMPC polymer series were examined by a differential scanning calorimeter (DSC) from −60 to 180 °C (Figure S7). Previous studies suggested that the Tg of the polymer would affect the crosslinking rate of BP derivatives. When the irradiation temperature was higher than Tg, the polymer would have sufficient free-volume to encounter surrounding C−H groups in the solid states. In contrast, when the irradiation temperature was lower than Tg, the segment motion would limit resulting in slow hydrogen abstraction.42 Based on DSC results, the Tg of BPMPC37, BPMPC55, BPMPC73, and BPMPC91 is 53.61, −0.98, 19.58, and 18.65 °C, respectively. The UV curing experiments were carried out under room temperature ≈25 °C, and the temperature at the irradiation spot is 49.2 °C, which was measured by an infrared thermometer. The Tg for all BPMPC polymers are lower or close to the irradiation temperature under continuous UV irradiation, which indicated that the polymer side chains have sufficient segmental movement, and the molecular motion is not the main reason for the difference in photocross-linking reactivity. The literature suggested that the photolysis in the polymer film follows a chemically controlled mechanism for T > Tg as in solution.33 In all BPMPC polymers, the monomer components are the same, but the concentration of each component is different. According to the previous studies, solvent conditions are an important parameter affecting the reactivity of BP derivatives. In simple terms, increasing the solvent polarity can shift the n−π* triplet to the π−π* or CT state, which has a lower reactivity, as compared to the former one. Therefore, BP derivatives demonstrated higher reactivity in the nonpolar solvent than in the polar solvent.15 In BPMPC polymers, as the amount of MPC side chain increases, the hydrophilicity, in other words, the polarity of the polymer would increase accordingly. The cross-linking kinetics results observed in BPMPC polymers were similar to BP derivatives in different solvent systems. More hydrophilicity of the polymer results in less reactivity of BP cross-linking. Therefore, a hypothesis arises that the hydrophilicity/polarity of the polymer matrix would affect crosslinking kinetics of BP pendent copolymers in a similar way as the solvent to BP derivatives.

To calculate the cross-linking rate constant for each polymer, the initial absorbance was normalized to 1 for all polymers, and the data were described by single-exponential decay.42
where \( k \) is the reaction rate constant, \( t \) is the irradiation time, and \( A_\infty \) is the constant absorbance in infinite time. According to the kinetics curves, the reaction constant, \( k \), was calculated, as shown in Table 2. A significant decrease in the value of the rate constant can be observed with the increase of MPC percentage. Figure 2 (bottom X axis, blue line) shows the relationship between the percentage of MPC and the kinetics constant, and a deceasing linear correlation can be observed.

### Table 2. Value of Rate Constant and log \( P \) of BPMPC Polymer Series

| Polymer     | BPMPC37 | BPMPC55 | BPMPC73 | BPMPC91 |
|-------------|---------|---------|---------|---------|
| \( k \) (10^{-2} \text{ s}^{-1}) | 7.65    | 4.16    | 2.50    | 1.30    |
| log \( P \) | 0.63    | -1.13   | -2.57   | -3.50   |

To further investigate the relationship between the polymer polarity and BP kinetics, octanol–water partition coefficients \( P \) were introduced. The value of log \( P \) of MPC, BMA, and 4-vinyl benzophenone (4-VBP) was -5.32, 2.81, and 4.24, respectively, which is consistent with the theory that a negative value of log \( P \) means the compound is more hydrophilic. The value of log \( P \) for each polymer was calculated based on eq 4, as listed in Table 2. The log \( P \) value decrease with the increase of MPC percentage, which indicated that the copolymer become more hydrophilic/polar. The relationship between log \( P \) and rate constant can be described as a linear correction (Figure 2, top X axis, red line) with a slope of 1.546 and intercept of 6.406 (eq 3), with a R-square of 0.98.

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k = 1.546 \times \log P + 6.404
\]

Up to this point, the hypothesis that the hydrophilicity/polarity of the copolymer would affect the cross-linking rate of the BP pendent group was valid when other factors were negligible.

To verify the hypothesis of the relationship between log \( P \) and kinetics coefficient, a series of MPC copolymers with different side chain lengths were synthesized and investigated. In the polymer matrix, the side chain length is also an important element that can influence many physical and chemical properties. A copolymer with the MPC monomer and quaternary amine was selected because of its antifouling and antimicrobial properties. At first, quaternized 2-(dimethylamino)ethyl methacrylate (DMAEMA) was synthesized by reflux DMAEMA with 1-bromobutane, 1-bromododecane, and 1-bromooctadecane, which have different lengths of carbon chains (Scheme 2A). The chemical structure of Q4, Q12, and Q18 were confirmed by 1H NMR. Radical polymerization was also used in the synthesis of MPC-Q polymers (Scheme 2B). The ratio of each monomer in MPC-Q was calculated based on the following analysis: 0.8−1.0 ppm (−CH3, 3H) for QDMAEMA unit; −3.34 ppm [−N(CH3)3, 9H and −N(CH3)2, 6H] for MPC and QDMAEMA units; and 6.80−7.85 ppm (BP-H, 9H) for the BP unit. The monomer ratio of MPC, QDMAEMA, and 4-VBP was fixed as 30, 60, and 10%, respectively. The monomer ratio in the products were slightly different from the input (Table 3). On the aspect of the chemical structure, the notable difference between these MPC-Q polymers is the length of the sidechain.

Kinetics of all MPC-Q polymers was also recorded by UV−vis (Figure S8), and the conversion of cross-linking was shown using the decrease of the BP absorbance peak as a function of irradiation time (Figure 3). As shown in Figure 3, MPC-Q18 has the fastest cross-linking rate followed by the MPC-Q12,
and MPC-Q4 has the slowest rate. The same single-exponential decay model was used to calculate the kinetics constant \( k \) for MPC-Q polymers, and the same equation was used for the calculation of the polymer log \( P \) value (Table 4). The log \( P \) value for Q4, Q12, and Q18 is \(-1.14, 2.90, \) and 5.93, respectively.

### Table 4. Rate Constant \( (k) \) for MPC-Q Polymers

| polymer          | MPC-Q4 | MPC-Q12 | MPC-Q18 |
|------------------|--------|---------|---------|
| \( k_{\text{calc}} \) \( \times 10^{-2} \) s\(^{-1} \) | 3.34   | 0.83    | 2.71    |
| \( k \) \( \times 10^{-2} \) s\(^{-1} \)   | 3.475  | 4.131   | 11.517  |

\( k_{\text{calc}} \) was generated by the eq 3 using the log \( P \) of the polymer and demonstrated outstanding predication for MPC-Q4 and MPC-Q18. However, the value of \( k_{\text{calc}} \) (MPC-Q8) is about twice the value of \( k \) from the UV-vis experiment.

To explain these results, the thermal properties of MPC-Q polymers were investigated by DSC. According to DSC traces (Figure S9), the \( T_g \) crystal transition temperature \( (T_g) \), and melting temperature \( (T_m) \) for MPC-Q4 are \(-1.88, \) and 133 °C, respectively; \( T_g \) for MPC-Q12 is 121 °C; and the \( T_g \) for MPC-Q18 is 12 °C. Although the \( T_g \) for MPC-Q18 was not detected in the measuring range \((-60 \) to 180 °C), a very low \( T_g \) can be anticipated based on the value of \( T_m \). MPC-Q4 and MPC-Q18 have a \( T_g \) lower than room temperature, which is similar to the situation of BPMPC, as discussed above. When \( T > T_g \), the cross-linking rate was mainly controlled by the chemical environment. Therefore, the relationship between BP reactivity and polymer hydrophilicity/polarity demonstrated a good fit for MPC-Q4 and MPC-Q18, and the rate constants calculated \( (k_{\text{calc}}) \) based on log \( P \) were very close to the experimental values. However, the \( T_g \) of MPC-Q12 is 121.28 °C, which is much higher than the temperature at irradiation spot. As a result, the chain segment movement in MPC-Q12 was restricted, and the BP photoreaction would not proceed as that found in solution. Hence, the experimental rate constant of MPC-Q12 was only half of the calculated value that only considered the chemical environment. The hypothesis of the linear correlation between log \( P \) and \( k \) is only effective for the zwitterionic copolymers with a relatively low \( T_g \) in which the kinetics was dominated by the hydrophilicity/polarity of the polymer matrix.

Substituent effects also play a significant role in influencing the kinetics of BP derivatives. Generally, electron-withdrawing groups increase the reactivity of n–π* radicals, while electron-donating groups have the opposite effect, inhibiting H-abstraction. To examine the influence of BP ring substitution on the zwitterionic copolymer, 4-acryloylbenzenophenone (ABP) and prop-2-ethyl-4-benzoylbenzonate (PBB) were synthesized with the opposite effect substituent (Scheme 3A,B). Poly(MPC-BMA-ABP) (ABPMPC) and poly(MPC-BMA-PBB) (PBMPB) were produced using the same procedure as BPMPC. The feeding ratio of MPC and BMA was fixed at 70 and 30% in three polymers, while the only difference is the substituent group on BP rings (Scheme 3C).

From the UV-vis spectra (Figure S10), ABPMPC with an electron-donating group demonstrated a slower cross-linking rate than BPMPC73, and PBMPB exhibited higher reactivity than BPMPC73 with an electron-withdrawing group. These results indicated that the substituent effects for BP kinetics are still effective for BP pendent copolymers and should be taken into consideration for the polymer designing.

## CONCLUSIONS

The BP cross-linking kinetics in BP pendent zwitterionic copolymers was investigated, and the factors that affect the reactivity were discussed in this work. The kinetics constant of BP photocross-linking demonstrated a linear relation with the value of polymer log \( P \) when the zwitterionic polymer has a \( T_g \) lower or close to the temperature of irradiation spot. As the reactivity of BP derivatives was significantly influenced by the polarity of solvent systems, the hypothesis that the hydrophilicity/polarity of the polymer matrix would affect the BP cross-linking reaction in polymer films was raised. Meanwhile, for the zwitterionic polymer with a higher \( T_g \), the segmental movement was restricted, the polymer thermal properties started to taking control of the reactivity, and the connection between the BP cross-linking kinetics and the log \( P \) of the zwitterionic polymer disappeared. Additionally, the substituents on BP in polymer side chains demonstrate similar effects to the cross-linking kinetics as in small molecules in solution, which implied that the cross-linking reactivity of BP derivatives might work in BP polymer films as well. As the development functional polymer utilizing the BP photoreaction, this work can provide some guidance to the functional polymer design and selection.

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**Table 3. Synthetic Results of MPC-Q Polymers**

| composition (mol/%) in feed MPC/QDMAEA/BP | initiator (mmol/mL) | composition (mol/%) in copolymer MPC/QDMAEMA/BP | yield (%) |
|--------------------------------------------|---------------------|-----------------------------------------------|----------|
| MPC-Q4 30/60/10                            | 0.02                | 27.5/66.8/5.7                                 | 75.6     |
| MPC-Q12 30/60/10                           | 0.02                | 26.0/68.5/5.2                                 | 67.8     |
| MPC-Q18 30/60/10                           | 0.02                | 27.5/64.9/7.6                                 | 72.3     |

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**Figure 3.** MPC-Q4–18 photocrosslinking kinetics study by UV-vis spectroscopy.
**EXPERIMENT SECTION**

**Materials.** MPC, diisopropylethylamine, N,N′-disopropylcarbodiimide (DIC), pyrene, and DMAEMA were purchased from Sigma-Aldrich, 2,2′-azobis(2-methylpropionitrile) (AIBN), 1-bromobutane (C4), 1-bromododecane (C12), allyl alcohol, 1-bromooctadecane (C18), and BMA were bought from Alfa-Aesar. Isobutyltrichlorosilane (iBTS), 4-hydroxybenzophenone, and 4-dimethylaminopyridine (DMAP) were purchased from Tokyo Chemical Industry. Acryloyl chloride was purchased from Beantown. 4-VBP42 and 4-benzoylbenzoic acid 48 were synthesized according to previous reports.

**Synthesis of ABP.** 4-Hydroxybenzophenone (20 g, 0.1 mol), diisopropylethylamine (19.3 mL, 0.11 mol), and dichloromethane (80 mL) were added into a round-bottom flask, and the solution was stirred in an ice bath. Acryloyl chloride (9.02 mL, 0.11 mol) solution in dichloromethane (20 mL) was added to the reaction dropwise. The reaction was carried out at 0 °C for 3 h and then at room temperature for 5 h. The solvent was removed by rotary evaporation, and the residue was washed with 20% HCl, saturated NaHCO3, and then dried over sodium sulfate. The white crystal product was generated and recrystallized in n-hexane with a yield of 91%. The structure of ABP was confirmed by 1H NMR (Figure S1): δ: 7.88 (2H); 7.80 (2H); 7.60 (1H); 7.49 (2H); 7.27 (2H); 6.65 (1H); 6.35 (1H), 6.07 (1H).

**Synthesis of PBB.** A mixture of 4-benzoylbenzoic acid (2.5 g, 11 mmol), DIC (2.5 mL, 16 mmol), DMAP (0.1 g, 0.8 mmol), and dry CH2Cl2 (25 mL) was stirred for 2 h at 20 °C (dimmed light). Allyl alcohol (10 mL) was added, and the mixture was stirred at 20 °C for 24 h. The mixture was evaporated, the residue was taken up in CH2Cl2, and then, the solution was washed with saturated NaHCO3 solution and H2O. The residue was purified by fast chromatography. 1H NMR (Figure S2): δ: 8.20–8.14 (2H); 7.85–7.79 (4H); 7.61(1H); 7.49 (2H), 6.05(1H); 5.44 (1H); 5.32 (1H); 4.86 (2H).

**Synthesis of BPMPC Polymer Series.** All BPMPC polymers were synthesized by radical polymerization using the same procedure reported.53 Generally, appropriate amounts of MPC, BMA, and 4-VB41 were dissolved in pure EtOH (the total monomer concentration: 1 mmol mL−1) with the initiator AIBN (0.01 mmol mL−1), and the solutions were degassed under argon for 30 min. The polymerization reactions were carried out under N2 flow at 60 °C for 16 h. The reactions were stopped by exposing the solution to air, cooled to room temperature. The polymers were precipitated in ethyl ether and dried under vacuum for 12 h to obtain the white solid products. The structure and monomer ratio are confirmed by 1H NMR in DMSO-d6 (Figure S3).

**Synthesis of Quaternary DMAEMA (QDMAEMA).** DMAEMA (3.37 mL) and appropriate bromoalkane (mole ratio: 1:1.2) were added to 15 mL EtOH, and the solution was reflux under 60 °C for 1 h and then at 68 °C for 3 h. The solvent was removed by a rotavapor. The solution was cooled to room temperature before adding diethyl ether (35 mL). The crystallized monomer was filtered out, washed with diethyl ether for 3 times, and dried in a vacuum oven at room temperature overnight. The chemical structure of the product QDMAEMA was confirmed by 1H NMR in DMSO-d6 (Figure S4). DMAEMA–C9H18 (Q4) yield: 72%, δ (DMSO-d6): 6.06 (1H), 5.75 (1H), 4.49 (2H), 3.67 (2H), 3.07(6H), 3.03 (2H), 1.89 (3H), 1.64 (2H), 1.27(2H), 0.91 (3H). DMAEMA–C13H25 (Q12) yield, 58%, δ (DMSO-d6): 6.06 (1H), 5.75 (1H), 4.50 (2H), 3.67 (2H), 3.07(6H), 3.03 (2H), 1.89 (3H), 1.65 (2H), 1.27(18H), 0.84 (3H). DMAEMA–C18H37 (Q12) yield, 58%, δ (CDCl3): 6.16 (1H), 5.70 (1H), 4.65 (2H), 3.67 (2H), 3.07(6H), 3.03 (2H), 1.96 (3H), 1.65 (2H), 1.26(30H), 0.88 (3H).

**Synthesis of MPC-QDMAEMA (MPC-Q) Polymers.** MPC, QDMAEMA, and 4-VBP (mole ratio 3:6:1) were dissolved in EtOH (total monomer concentration: 1 mmol mL−1) with the initiator AIBN (0.02 mmol mL−1). The solution was degassed under argon for 30 min and then polymerized under N2 flow for 16 h under 60 °C. The polymer
was collected by precipitating in tetrahydrofuran and then kept under vacuum at room temperature overnight. White product was received, and $^1$H NMR was carried out to confirm the composition (Figure S5).

**Kinetics Measurement and Polymer Properties.** The crosslinking kinetics of all polymers were investigated using UV–vis spectroscopy on iBTS functionalized quartz substrates. The quartz slides were sonicated in deionized water, isopropanol, and acetone for 5 min each, followed by plasma (Harrick Plasma PDC-32G) cleaning and treatment with iBTS in toluene (10 mmol) overnight before modification with the polymer. The polymer solution (10 μL, 10 mg mL$^{-1}$) was cast on alkylated quartz, and the solvent was allowed to evaporate. The UV–vis spectroscopy was performed on a Cary Bio spectrophotometer (Varian). The UV light source was a Compact UV lamp (UVP) with the wavelength at 254 nm. The substrates were held at a certain distance from the light source during irradiation to obtain the power of 6.5 mW cm$^{-2}$. The substrates were held at a certain distance from the light source during irradiation to obtain the power of 6.5 mW cm$^{-2}$. The $T_g$ of the copolymer was measured using a DSC 250 (TA Instruments). Data were stored and manipulated using the software TRIOS v4.4 (TA Instruments). Samples were scanned at a rate of 10 °C min$^{-1}$, and the second-heat-scan curves were used for analysis.

The value of $P$ for each monomer was estimated using the Molinspiration online property calculation toolkit (http://www.molinspiration.com), which was based on group contributions and correction factors. The copolymer log $P$ was calculated based on the weighted average (mole percentage) of each component (eq 4).

$$P(\text{copolymer}) = \sum \text{mol \%} \times P(\text{monomer})$$

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**REFERENCES**

(1) Tanaka, Y.; Bond, M. R.; Kohler, J. J. Photocrosslinkers illuminate interactions in living cells. *Mol. BioSyst.* 2008, 4, 473–480.
(2) Pham, N. D.; Parker, R. B.; Kohler, J. J. Photocrosslinking approaches to interactome mapping. *Curr. Opin. Chem. Biol.* 2013, 17, 90–101.
(3) Nam, C.-Y.; Qin, Y.; Park, Y. S.; Hliaing, H.; Lu, X.; Ocko, B. M.; Black, C. T.; Grubbs, R. B. Photo-Cross-Linkable Azide-Functionalyzed Polyiophiene for Thermally Stable Bulk Heterojunction Solar Cells. *Macromolecules* 2012, 45, 2338–2347.
(4) Yoo, M.; Kim, S.; Lim, J.; Kramer, E. J.; Hawker, C. J.; Kim, B. J.; Bang, J. Facile Synthesis of Thermally Stable Core-Shell Gold Nanoparticles via Photo-Cross-Linkable Polymeric Ligands. *Macromolecules* 2010, 43, 3570–3575.
(5) Guo, L.-W.; Grant, J. E.; Hajiipour, A. R.; Muradov, H.; Arabian, M.; Artemyev, N. O.; Ruoho, A. E. Asymmetric interaction between rod cyclic GMP phosphodiesterase gamma subunits and alpha beta subunits. *J. Biol. Chem.* 2005, 280, 12585–12592.
(6) Suga, T.; Konishi, H.; Nishide, H. Photocrosslinked nitroxide polymer cathode-active materials for application in an organic-based paper battery. *Chem. Commun.* 2007, 1730–1732.
(7) Dankbar, D. M.; Gauglitz, G. A study on photoinitators used for biomolecule attachment to polymer surfaces. *Anal. Bioanal. Chem.* 2006, 386, 1967–1974.
(8) Allen, N. S.; Marin, M. C.; Edge, M.; Davies, D. W.; Garrett, J.; Jones, F.; Navaratnam, S.; Parsons, B. J. Photochemistry and photoinduced chemical crosslinking activity of type I & II co-reactive photoinitiators in acrylated prepolymer. *J. Photochem. Photobiol., A* 1999, 126, 135–149.
(9) Carroll, G. T.; Sojka, M. E.; Lei, X.; Turro, N. J.; Koberstein, J. T. Photoactive additives for cross-linking polymer films: Inhibition of dewetting in thin polymer films. *Langmuir* 2006, 22, 7748–7754.
(10) Dotcheva, M.; Dotcheva, D.; Stamenova, R.; Orohavots, A.; Tsvetanov, C.; Leder, J. Ultraviolet-induced crosslinking of solid poly(ethylene oxide). *J. Appl. Polym. Sci.* 1997, 64, 2299–2307.
(11) Pappas, S. P.; Fischer, R. M. Photochemistry of Pigments - Studies on Mechanism of Chalking. *J. Paint Technol.* 1975, 4, 3–10.
(12) Qu, B.; Xu, Y.; Ding, L.; Ranby, B. A new mechanism of benzophenone photoreduction in photoinitiated crosslinking of polyethylene and its model compounds. *J. Polym. Sci., Part A: Polym. Chem.* 2000, 38, 1005–1007.
(13) Ruhe, J.; Madge, D. Grafting of polymers to solid surfaces using self-assembled monolayers with polymerizable groups. *Albtr. Pap. Am. Chem. Soc.* 2003, 225, U684.
(14) Ruhe, J.; Seidel, K.; Toomey, R. Surface-attached polymer networks: Synthesis and swelling behavior. *Albtr. Pap. Am. Chem. Soc.* 2004, 227, U861.
(15) Dormán, G.; Nakamura, H.; Pulsipher, A.; Prestwich, G. D. The Life of Pi Star: Exploring the Exciting and Forbidden Worlds of the Benzophenone Photophore. *Chem. Rev.* 2016, 116, 15284–15398.
(16) Demeter, A.; László, B.; Bérces, T. Kinetics of Key Radical Reactions Occurring in the Photoreduction of Benzophenone by Isopropyl Alcohol. *Ber. Bunsen Phys. Chem.* 1988, 92, 1478–1485.
(17) Shoue, L. C. T.; Huie, R. E. Reactions of triplet decafluoro-phenylcyclohexene with allenes. A laser flash photolysis study. *J. Phys. Chem. A* 1997, 101, 3467–3471.
(18) Porter, G.; Suppan, P. Primary Photochemical Processes in Aromatic Molecules I2. Excited States of Benzophenone Derivatives. *Trans. Faraday Soc.* 1965, 61, 1664–1673.
(19) Bhaskuttan, A. C.; Singh, A. K.; Palit, D. K.; Sapre, A. V.; Mittal, J. P. Laser flash photolysis studies on the monohydroxy derivatives of benzophenone. *J. Phys. Chem. A* 1998, 102, 3470–3480.
(20) Singh, A. K.; Bhaskuttan, A. C.; Palit, D. K.; Mittal, J. P. Excited-state dynamics and photophysical properties of para-aminobenzophenone. J. Phys. Chem. A 2000, 104, 7002–7009.
(21) Ghoneim, N.; Monbelli, A.; Pilloud, D.; Suppan, P. Photochemical reactivity of para-aminobenzophenone in polar and nonpolar solvents. J. Photochem. Photobiol., A 1996, 94, 145–148.
(22) Li, W.; Xue, J.; Cheng, S. C.; Du, T.; Phillips, D. L. Influence of the chloro substituent position on the triplet reactivity of benzophenone. J. Raman Spectrosc. 2012, 43, 774–780.
(23) Aspari, P.; Ghoneim, N.; Haselbach, E.; von Raumer, M.; Suppan, P.; Vauthey, E. Photoinduced electron transfer between triethylamine and aromatic carbonyl compounds: The role of the nature of the lowest triplet state. J. Chem. Soc., Faraday Trans. 1996, 92, 1689–1691.
(24) Turro, N. J. R. V.; Scaino, J. C. Principles of Molecular Photochemistry: An Introduction; University Science Books: Herendan, VA, 2009.
(25) Sergentu, D.-C.; Maurice, R.; Havenith, R. W. A.; Broer, R.; Roca-Sanjua, D. Computational determination of the dominant triplet population mechanism in photoexcited benzophenone. Phys. Chem. Chem. Phys. 2014, 16, 25393–25403.
(26) Katchalsky, A.; Künzle, O.; Kuhn, W. Behavior of Polycvalent Polymeric Ions in Solution. J. Polym. Sci. 1950, 5, 283–300.
(27) Kuhn, W.; Kunze, O.; Katchalsky, A. Denouement De Molecules En Chaines Polynvalentes Par Des Charges Electriques En Solution. Bull. Soc. Chim. Belg. 1948, 57, 421–431.
(28) Kunze, O. Einfluss Mittlerer Ionenkonzentrationen Auf Die Elektrostatische Energie Von Fadenmolekulein in Losung. Recl. Trav. Chim. Pays-Bas 1949, 68, 699–716.
(29) Kuhn, W.; Hargitay, B.; Katchalsky, A.; Eisenberg, H. Reversible Dissolution and Contraction by Changing the State of Ionization of High-Polymer Acid Networks. Nature 1950, 165, 514–516.
(30) Eisenbach, C. D. cis-Trans Isomerization of Aromatic Azocompounds Built in the Polyester Segment of Poly(Ester Uretahanes). Polym. Bull. 1979, 1, 517–522.
(31) Menjú, A.; Hayashi, K.; Irie, M. Photoresponsive Polymers. 3. Reversible Solution Viscosity Change of Poly(Methacrylic Acid) Having Spirobenzopyran Pendant Groups in Methanol. Macromolecules 1981, 14, 755–758.
(32) Horie, K.; Mita, I.; Fujita, H. Reactions and Photodynamics in Polymer Solids. Adv. Polym. Sci. 1989, 88, 77–128.
(33) Horie, K.; Morishita, K.; Mita, I. Photochemistry in Polymer Solids. 3. Kinetics for Nonexponential Decay of Benzophenone Phosphorescence in Acrylic and Methacrylic Polymers. Macromolecules 1984, 17, 1746–1750.
(34) Szczupak, B.; Ryder, A. G.; Togashi, D. M.; Klymchenko, A. S.; Rochev, Y. A.; Gorelov, A.; Glynn, T. J. Polarity Assessment of Thermoresponsive Poly(NIPAM-co-NtBA) Copolymer Films Using Fluorescence Methods. J. Fluoresc. 2010, 20, 719–731.
(35) Sangster, J. Octanol-Water Partition-Coefficients of Simple Organic-Compounds. J. Phys. Chem. Ref. Data 1989, 18, 1111–1229.
(36) Bodor, N.; Gabanyi, Z.; Wong, C. K. A New Method for the Estimation of Partition-Coefficient. J. Am. Chem. Soc. 1989, 111, 3783–3786.
(37) Miller, M. M.; Wasik, S. P.; Huang, G. L.; Shiu, W. Y.; Mackay, D. Relationships between Octanol Water Partition-Coefficient and Aqueous Solubility. Environ. Sci. Technol. 1985, 19, 522–529.
(38) Ertl, P.; Rolhe, B.; Selzer, P. Fast calculation of molecular polar surface area as a sum of fragment-based contributions and its application to the prediction of drug transport properties. J. Med. Chem. 2000, 43, 3714–3717.
(39) Demeter, A.; Horváth, K.; Böör, K.; Molnár, L.; Soós, T.; Lendvay, G. Substituent Effect on the Photoresponse Kinetics of Benzophenone. J. Phys. Chem. A 2013, 117, 10196–10210.