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Wavelength Flexibility in Photoinitiated Cationic Polymerization

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Summary: The spectral sensitivity of onium salt photoinitiators in cationic polymerization can be tuned from the short wavelength region of the UV spectrum to wavelengths up to the visible region by using direct and indirect activation, respectively. Indirect activation is based on the electron transfer reactions between onium salts and free radical photoinitiators, appropriate sensitizers and compounds capable of forming charge transfer complexes. Bisacylphosphine oxides, dimanganese decacarbonyl in conjunction with alkyl halides and titanocene type photoinitiators such as Irgacure 784 were shown to be useful free radical promoters providing the possibility of performing cationic polymerization in the long wavelength and visible region. The synthetic routes to prepare block copolymers by using electron transfer photosensitization and free radical promoted cationic polymerization are also described.

Keywords: electron transfer; long wavelength; onium salts; photoinitiated cationic polymerization; spectral sensitivity

Introduction

Photoinitiated cationic polymerization is an important industrial process widely used in different applications such as coatings, inks, adhesives and photolithography[1, 2]. Photoinitiated cationic polymerization can be initiated by onium salts such as diaryliodonium[3,4] triarylsulphonium[5] and alkoxypyridinium[6-8]. Photolysis of these salts leads to the formation of reactive cations or Brønsted acids which react efficiently with monomers such as vinyl ethers and cyclic ethers.

Photoinitiated cationic polymerization by direct irradiation of simple onium salts can be performed usually below 300 nm. This brings some limitations on the potential uses of cationic polymerization particularly when visible light emitting light sources are used. Chemical attachment of chromophoric groups onto aromatic groups of the salts is one way to broaden the spectral sensitivity of the onium salts. However, it requires multistep synthetic procedures and the

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desired shift in the absorption characteristics of the salts could still not be achieved. Several indirect ways to overcome this problem have been described[9]. All of these pathways involve electron transfer reactions either with photoexcited sensitizer [10-14] or free radicals[15- 18] and with the electron donor compounds in the excited charge transfer complexes[19].

This paper provides an overview of indirect ways for providing working conditions for photoinitiated cationic polymerization at a broad wavelength range. Special emphasis will be placed on the use of organic and organic-inorganic hydride-free radical sources such as bisacylphosphine oxides, and manganese decacarbonyl and titanocene type photoiniators, respectively.

Photosensitized Cationic Polymerization

The absorption characteristics of the onium salt based photoinitiating systems can be adapted for particular applications requiring activation at wavelengths between 330-650 nm by the use of various photosensitizers. Numerous photosensitizers were found to be effective in inducing onium salt decomposition by the electron transfer reaction as depicted in reaction (1) (Table 1). Notably, aromatic carbonyl photosensitizers which undergo electron transfer via a radical route are not included[15, 20].

$$(PS^*) + On^+ \longrightarrow PS^{+\bullet} + On\bullet \qquad (1)$$

The photosensitizer radical cations initiate the cationic polymerization directly. Alternatively, they undergo hydrogen abstraction yielding substituted photosensitizer and Brønsted acid capable of initiating cationic polymerization.

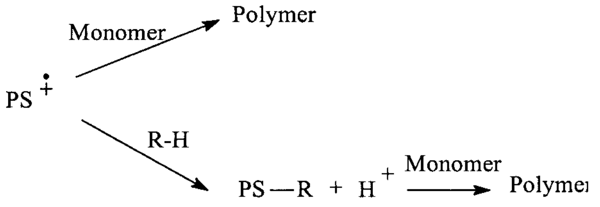

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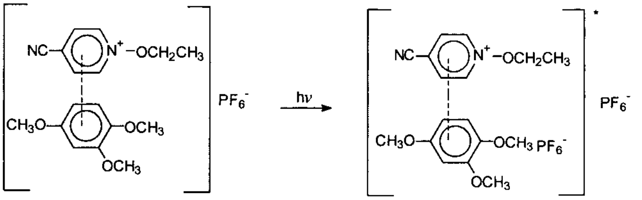
Table 1. Electron transfer photosensitizers used in photoinitiated cationic polymerization

Photosensitizer	Reference
Anthracene	10-12
Perylene	21-23
Phenothiazine	14, 21-24
Pyrene	21
Carbazole and derivatives	25-26

Photoinitiated Cationic Polymerization by Charge Transfer Complexes

It has been shown[19] that charge transfer complexes formed by mixing certain pyridinium ions with aromatic electron donors act as photoinitiators for cationic polymerization. It was suggested that radical cations of donors, formed by excitation of CT complex according to the following mechanism, are responsible for the polymerization. Once the radical cations are formed, the initiaton than proceeds in a similar way to that described above for the photosensitizer radical cations.



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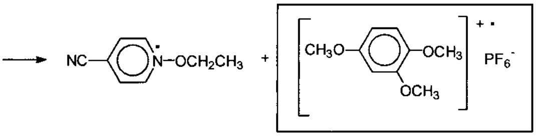

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Depending on the structure of the electron donor compound and the acceptor pyridinium salt the absorption bands of the charge transfer complexes lie in the range between 350-650 nm. Therefore, the polymerizations can practically be performed at these wavelengths. Interestingly, CT initiation can be realized only with alkoxy pyrdinium salts. The iodonium and sulphonium salts either do not form such complexes or their complexes absorb at lower wavelengths.

Free Radical Promoted Cationic Polymerization

Among the indirectly acting initiating systems, free radical promoted cationic polymerization is the most flexible route, since free radical photoinitiators with a wide range of absorption characteristics are available. Many photochemically formed radicals[27-32] can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization according to the following reactions.

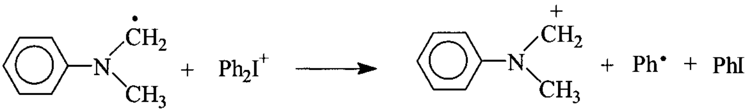
$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{R}\bullet \tag{6}$$

$$\mathrm{R}\bullet \xrightarrow{\mathrm{On}^{+}} \mathrm{R}^{+} + \mathrm{On}\bullet \tag{7}$$

$$\mathrm{R}^{+} \xrightarrow{\mathrm{M}} \mathrm{Polymer} \tag{8}$$

The use of visible light free radical photoinitiators

Although the use of many photoinitiators in free radical promoted cationic polymerization has been described, the sensitivity of the initiating system could be only rarely extended to the region of visible light. In a recent study[33], radicals formed by the irradiation system containing a xanthen dye and an aromatic amine, were oxidized by a diaryliodonium salt. By using the dye, the wavelengths of incident light chosen were between 500 and 650 nm. The initiation mechanism is assumed to involve the oxidation of α-amino radicals formed after hydrogen abstraction to the respective cations, which initiate the polymerization.



(9)

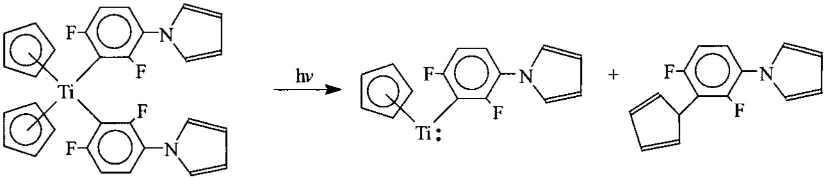
More recently, a novel visible light initiating system for the cationic polymerization of cyclic ethers such as cyclohexene oxide (CHO) and alkyl vinyl ethers such as butyl vinyl ether (BVE) was described[34]. This system consists of an organic halide, namely halogen containing solvents, dimanganese decacarbonyl, $Mn_2(CO)_{10}$, and an onium salts such as diphenyl iodonium salt, $Ph_2I^+PF_6^-$. Radical generation was achieved upon irradiation of $Mn_2(CO)_{10}$ in the presence of organic halide at λ = 436 nm where the onium salt is transparent. The proposed initiation mechanism, in which solvent methylene chloride and diphenyl iodonium salt were used as organic halide and oxidant, respectively, is shown below.

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\,Mn(CO)_5 \qquad (10)$$

$$CH_2Cl_2 + Mn(CO)_5 \longrightarrow \dot{C}H_2Cl + Mn(CO)_5Cl \qquad (11)$$

$$\dot{C}H_2Cl + Ph_2I^+PF_6^- \longrightarrow \overset{+}{C}H_2Cl\,\overset{-}{PF_6} + PhI + Ph\bullet \qquad (12)$$

Both systems consisted of three components for the generation of reactive cations, and the initiation mechanisms are rather complex. However, titanocene derivatives represent one of the few examples of the one component systems directly activated upon photolysis to initiate free radical polymerization[36]. Titanocene type photoinitiator, namely Irgacure 784, was also tested for its suitability as a visible light free radical source in free radical promoted cationic polymerization. For this purpose, cyclohexene oxide (CHO) was polymerized with combination of Irgacure 784 and an onium salt. CHO was polymerized effectively with iodonium and N-alkoxy pyridinium salts. Simple triaryl sulphonium salts do not undergo radical induced decomposition due to the unfavorable redox potentials. Notably, the two components of the initiating system are indispensable for the polymerization to occur; no polymer is formed in the absence of one of the compounds under our reaction conditions. When a proton scavenger, 2,6di-tert-butyl-4-methylpyridine, was present in the reaction mixture, no polymer was formed during irradiation indicating that protons act as initiators. Photodecomposition behavior of titanocene derivatives is related to their structure. Radical trapping experiments revealed that non-fluorinated diaryl titanocenes photodecompose via homolytic cleavage of the metal-aryl-ligand bond to generate aryl and titanocene radicals. It is known that fluorinated titanocene derivatives such as Irgacure 784 yield no primary organic radicals, but rather, titanium centered diradicals according to the following reaction.



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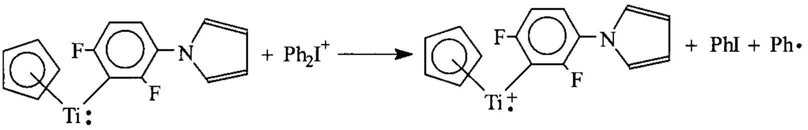
In the presence of suitable oxidants such as onium salts, these biradicals may undergo electron transfer reaction to yield radical cations.



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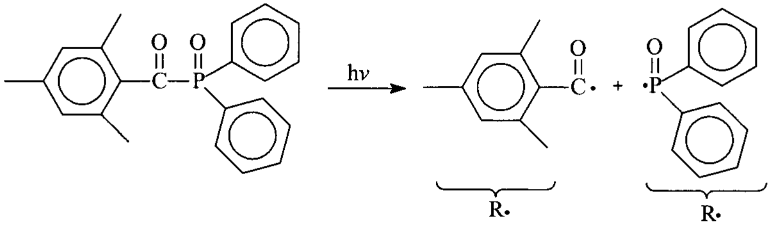
The possibility of direct initiation by radical cations thus formed is precluded by spectroscopic investigations and absence of polymerization in the presence of a proton scavenger. Although how the protons are generated is not known at present, these results suggest that they played an important role in the initiation

The use of bisacylphosphine oxides

The value of acylphosphineoxides absorbing UV light at around 380 nm has been reported for free radical promoted cationic polymerization[27]. However, in spite of their high performances, these photoinitators are only active when the photochemically generated benzoyl and phosphonyl radicals undergo addition or abstraction reactions[28] with monomer. The resulting carbon centered radicals are converted to carbocations by reaction with Ph_2I^+ ions.



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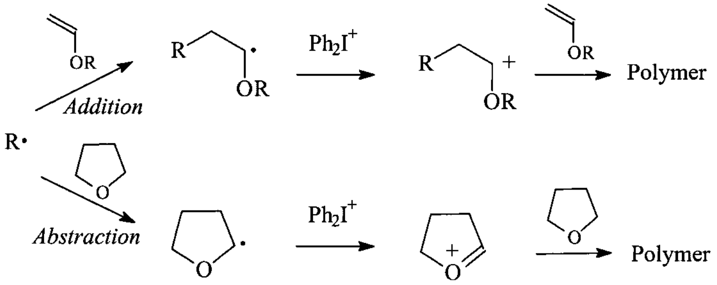

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Therefore, their use in technical applications requiring monomers, which are unreactive towards photochemically generated radicals, is impossible. In an effort to overcome these limitations, we have recently reported[37] the use bisacylphosphine oxides that are especially appropriate in free radical promoted cationic polymerization. By introducing another benzoyl substituent adjacent to the phosphonyl group, the absorption is shifted to longer wavelengths. Moreover, the radicals formed from biscaylphosphine oxides were shown to be oxidizable directly without the necessity of the reaction with the monomer. The structure of bisacylphosphineoxides used successfully in free radical promoted cationic polymerization is given below.

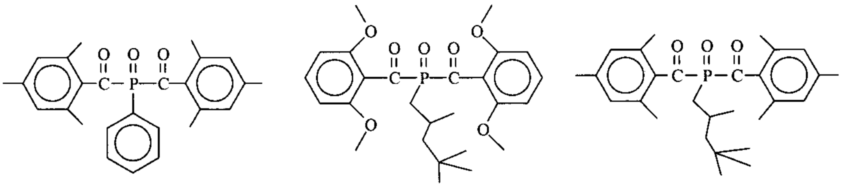
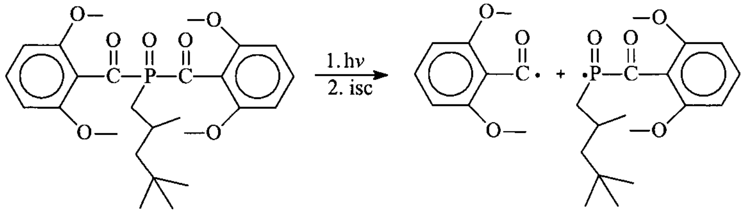


Chart 1. The structures of bisacylphosphineoxides used in free radical promoted cationic polymerization

In general, radicals with electron donating groups undergo oxidation more favorably and are therefore more efficient in free radical promoted cationic polymerization. However, phosphinoyl radicals formed from bisacylphosphine oxides according to reaction (18) possess electron withdrawing benzoyl substituents, and their reactivity should be lower than those formed from monoacylphosphineoxide (see reaction 5). Contradictorily, the bisacylphosphineoxides perform significantly better than with monoaclyphosphine oxide. This better performance was correlated with p-character on the phosphorous atom as reflected by the ^{31}P hyperfine coupling constant.



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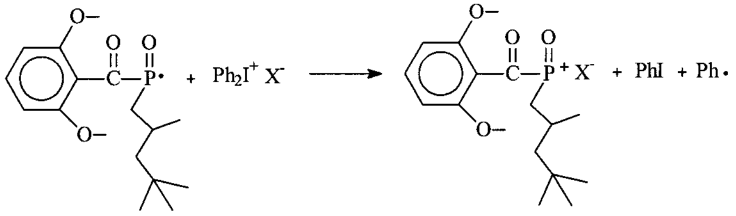
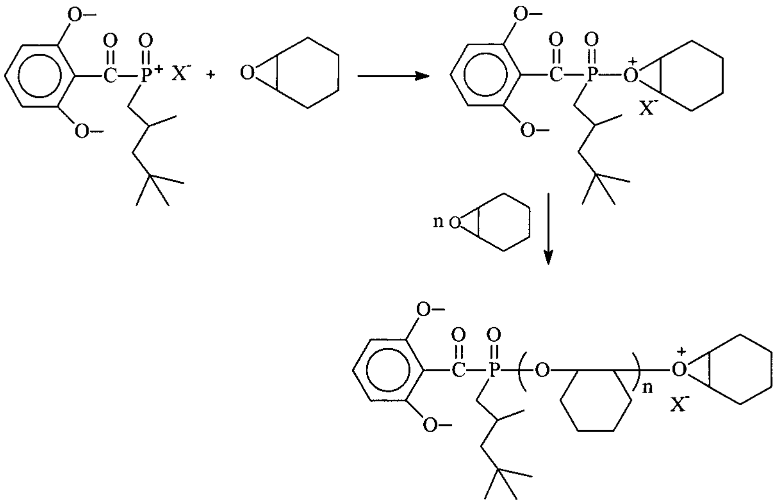


(19)

It follows that phosphonium ions formed according to the reaction (19) must be capable of initiating the cationic polymerization, as illustrated in reactions (20) and (21), using cyclohexene oxide (CHO) as an example monomer. In this case, poly(cyclohexene oxide) chains with attached benzoylphosphinoyl groups should be formed. Indeed, ^{1}H-NMR measurements revealed, apart from aliphatic protons, also existence of aromatic protons in the polymer.



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The use of free radicals generated by hydrogen abstraction

Oxidizable radicals can also be formed from the hydrogen abstraction reaction of photoexcited aromatic carbonyl compounds. In this case, the singlet photoexcited sensitizer undergoes successive intersystem crossing, hydrogen abstraction and electron transfer reactions to yield Brønsted acids which are responsible for the initiation.

$$Ar_2C{=}O \xrightarrow{h\nu} \left[Ar_2C{=}O\right]^1 \xrightarrow{i.s.c.} \left[Ar_2C{=}O\right]^3 \quad (22)$$

$$\left[Ar_2C{=}O\right]^3 + R\text{-}H \longrightarrow Ar_2\overset{\bullet}{C}\text{-}OH + R \quad (23)$$

$$Ar_2\overset{\bullet}{C}\text{-}OH + On^+ \longrightarrow Ar_2\overset{+}{C}\text{-}OH + On\bullet \quad (24)$$

$$Ar_2\overset{+}{C}\text{-}OH \longrightarrow Ar_2C{=}O + H^+ \quad (25)$$

$$H^+ + \text{Monomer} \longrightarrow \text{Polymer} \quad (26)$$

By using appropriate sensitizers such as benzophenone, thioxanthone, camphorquinone, benzil and antraquinone derivatives, the wavelength flexibility for the initiation could be achieved in the range of 350-485 nm.

Table 2. Hydrogen abstraction type photosensitizers used in free radical promoted cationic polymerization

Photosensitizer	λ_{max} (nm)[a]	Ref.
Benzophenone	340	7, 15, 16
Thioxanthone	380	10, 11
Benzil	480-486.5	7, 20
Camphorquinone	478	20
2-ethylanthraquinone	325	20

[a]In CH_2Cl_2

Block Copolymers by Photoinitiated Cationic Polymerization Involving Electron Transfer Reactions

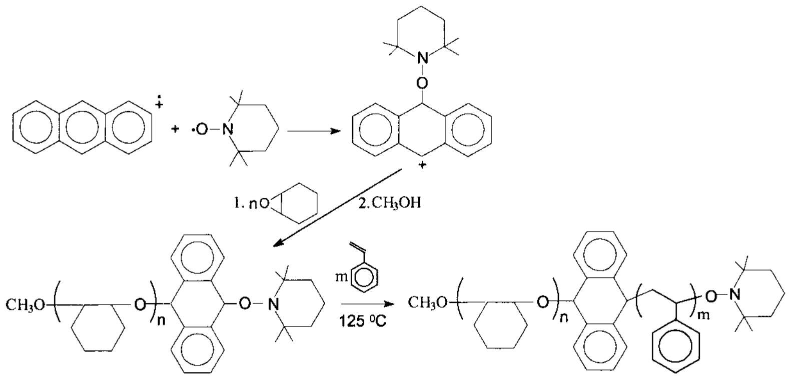
Although photoinitiating systems described above have the lack of polymerization control, they still contribute to the macromolecular engineering of synthetic polymers. For example, block copolymers can be prepared by using polymeric photoactive molecules, i.e., molecules capable of acting as electron transfer sensitizer or free radical initiator[38]. These systems consist of a photochemical reaction followed by an electron transfer by which active cations are produced at the chain ends, which themselves initiate the polymerization of a second monomer. Low temperature conditions, usually room temperature, prevent side reaction leading to the formation of homopolymers, and high block yields are attained. Table 3 contains a summary of the types of block copolymers prepared using photoinduced cationic polymerization based on electron transfer reactions.

Early examples were undertaken to show that different polymerization techniques could be combined with photoinduced cationic polymerization. However, recent examples illustrate that living methods like nitroxide mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP) could also used in the controlled synthesis of block copolymers.

Table 3. Summary of block copolymers prepared using photonoinitiated cationic polymerization involving electron transfer reactions

Type of photoinitiated cationic polymerization	Block Copolymer	Ref.
Free radical promoted	Polytetrahydrofuran-*b*-polystyrene	18
Free radical promoted	Polystyrene-*b*-poly(butyl vinyl ether)	39
Free radical promoted	Poly(phenylmethylsilane)-*b*-poly(cyclohexene oxide)	32, 40
Free radical promoted	Polystyrene-*b*-poly(cyclohexene oxide)	41, 42
Free radical promoted	Poly(ε-caprolactone)-*b*-poly(cyclohexene oxide)	42
Free radical promoted	Poly(*p*-methoxystyrene)-*b*-poly(cyclohexene oxide)	43
Free radical promoted	Poly(methyl methacrylate)-*b*-poly(butyl vinyl ether)	40
Photosensitized electron transfer	Polytetrahydrofuran-*b*-poly(cyclohexene oxide)	11
Photosensitized electron transfer	Polytetrahydrofuran-*b*-poly(methyl methacrylate)	44
Photosensitized electron transfer	Poly(cyclohexene oxide)-*b*-polystyrene	45
Photosensitized electron transfer	Polyurethane-*b*-polytetrahydrofuran	46

For example, photoexcited anthracene was reacted[45] with an alkoxy pyridinium salt, which produced a radical cation that could be trapped with TEMPO to create a dual initiating species capable of both cationic polymerization and NMP. After the polymerization of CHO, the macroinitiator was purified and used for the polymerization of styrene. The resulting block copolymers had increased molecular weights (Mn=3200 to 40000) with no increase in the molecular weight distribution (Mw/Mn=1.5).

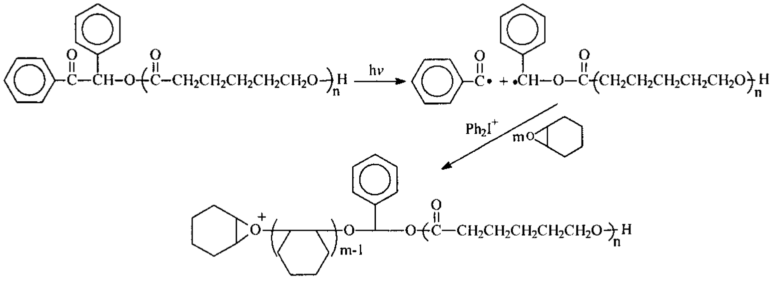


(27)

(28)

(29)

Like low molar mass analogs, electron donating polymeric radicals may conveniently be oxidized to polymeric carbocations to promote cationic polymerization of cyclic ethers. We have recently demonstrated[42] that irradiation of end-chain or midchain benzoin-functionalized polymers, in conjunction with onium salts as oxidants in the presence of cationically polymerizable monomers, makes it possible to synthesize block copolymers as illustrated below for the example of poly(ε-caprolactone)-*b*-poly(cyclohexene oxide).



(30)

(31)

Because the initial photoactive polymers were prepared by controlled polymerization methods such as ATRP or ROP, and the fact that the side reactions are limited in the photoinitiated cationic polymerization step, block copolymers with relatively low polydispersites were formed.

Conclusion

It has been shown that the indirect activation of onium salts based on electron transfer with various additives can be used to initiate cationic polymerization, with the decisive advantage of a photosensitivity range extending up to the visible range. Moreover, the initiating characteristics of such systems favors of the development of novel synthetic procedures for block copolymers with complex structures formed from different monomers.

Acknowledgement

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