Initiation Of Cationic Polymerization Induced By Photogenerated Radicals

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Summary

Mechanistic details concerning cationic polymerization induced by photogenerated radicals are discussed. This method pertains to the generation of reactive carbocations via oxidation of electron-donor radicals, formed upon irradiation, by onium salts. Moreover, the use of electron transfer processes in free radical polymerizing systems are described. Possibilities for preparing block copolymers by free radical promoted cationic polymerization are also described.

Introduction

Although most technically applied UV curing processes are based on free radical polymerization[1], ionic photopolymerization also holds considerable promise in many applications. Photoinduced cationic polymerization is also particularly attractive[2] because of the wide breadth of chemical and physical properties which can be realized through the polymerization of compounds of quite different chemical nature such as expoxides, sulfides, lactones, silicons, etc. Further, many monomers that are prone to cationic polymerization are of low volatility, negligible toxicity and possess good rheological properties. Molecular oxygen does not inhibit polymerization. Thermally stable onium salts such as diaryliodonium and triarylsulphonium salts ($Ar_2I^+X^-$ and $Ar_3S^+X^-$ with $X^- = PF_6^-$, AsF_6^- and SbF_6^-) are well established[3] photoinitiators for cationic polymerization. The direct absorption of light by the onium ion results in the cleavage of C-I or C-S bonds, respectively[4]. In the presence of H-donors, such as the solvent, Bronsted acids capable of initiating cationic polymerization, are formed. Recently, evidence was obtained[5] for cationic radicals, formed as tran-

sients, also being capable of initiating cationic polymerization.

Why do we utilize free radical photoinitiators in cationic polymerization?

Most commercial medium and high pressure mercury arcs provide substantial emission in the 300-400 nm spectral region[6]. Iodonium and sulphonium salts have very poor absorptivity at these wavelengths, which strongly reduces the practical application of onium salts as photoinitiators for cationic polymerization. Therefore, the use of suitable "free radical promoters" absorbing at 300-400 nm and, thereby, decomposing into free radicals, which readily react with onium ions by an electron transfer process, according to reaction (1) was suggested[7]. Other types of sensitization have already been discussed by Pappas, et al.[8].

(1) $$R\cdot + On^+ \longrightarrow R^+ + On\cdot$$
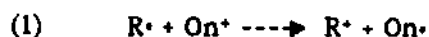
For efficient electron transfer, the free energy change (ΔG), which may be estimated from equation (2), must be negative.

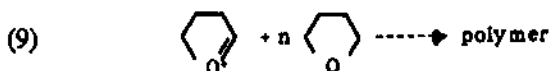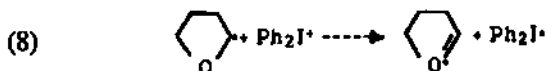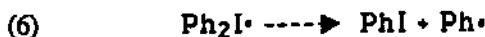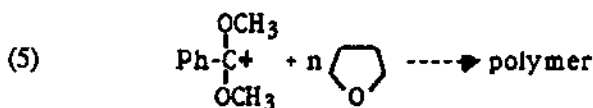(2) $$\Delta G - 97 \left[E^{ox}_{1/2}(R\cdot) - E^{red}_{1/2}(On^+) \right]$$

Carbon centered radicals possessing electron donor groups such as alkoxy and hydroxy groups have low reduction potentials which ease the electron transfer process. Similarly, the effectiveness of onium salts, for example, is related to their electron acceptability[9], ArN_2+ ($E^{red}_{1/2}=0.29$ V) > Ar_2I^+($E^{red} = 0.2$V) > Ar_3S^+ ($E^{red}_{1/2}=-1.2$V). Aryldiazonium salts are most suitable for electronic transfer from radicals but suffer from thermal instability. Triarylsulphonium salts do not participate[10] efficiently in this process due to the less favorable reduction potential. Therefore, for practical purposes only diaryliodonium salts may conveniently be used in

the initiation of cationic polymerization induced by photogenerated radicals.

2-2-Dimethoxy-2-phenyl acetophenon (DMPA)-iodonium salt system.

Photoinitiated cationic polymerization of tetrahydrofuran (THF) using iodonium salt and DMPA with light of wavelength at 366 nm has been studied in detail[11] and shown to involve quantum yields for initiation of about 30. This implies that 30 cationic chains are started for every excited molecule of DMPA. Amplification of photons results from radical chain reaction as shown below.

(3) $$Ph-\overset{O}{\underset{}{C}}-\overset{OCH_3}{\underset{OCH_3}{C}}-Ph \overset{h\nu}{----\blacktriangleright} Ph-\overset{O}{\underset{}{C}}\cdot + Ph-\overset{OCH_3}{\underset{OCH_3}{C}}\cdot$$

(4) $$Ph-\overset{OCH_3}{\underset{OCH_3}{C}}\cdot + Ph_2I^+ ----\blacktriangleright Ph-\overset{OCH_3}{\underset{OCH_3}{C}}^+ + Ph_2I\cdot$$

(5) $$Ph-\overset{OCH_3}{\underset{OCH_3}{C}}^+ + n\underset{O}{\bigcirc} ----\blacktriangleright polymer$$

(6) $$Ph_2I\cdot ----\blacktriangleright PhI + Ph\cdot$$

(7) $$Ph\cdot + \underset{O}{\langle\rangle} ----\blacktriangleright Ph-H + \underset{O}{\langle\rangle}\cdot$$

(8) $$\underset{O}{\langle\rangle}\cdot + Ph_2I^+ ----\blacktriangleright \underset{O}{\langle\rangle}^+ + Ph_2I\cdot$$

(9) $$\underset{O}{\langle\rangle}^+ + n\underset{O}{\langle\rangle} ----\blacktriangleright polymer$$
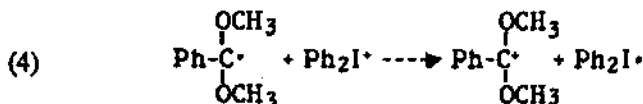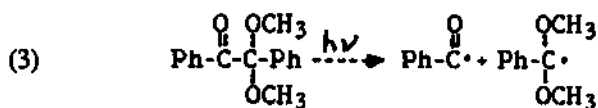
The important reactions of this process are light induced generation of free radicals (reaction 3), oxidation of radicals to corresponding carbocations by the reduction of the iodonium salt (reaction 4), regeneration of radicals in a chain process, involving H-abstraction from monomer (reaction 7) by phenyl radicals from dissociation of diphenyliodo radical (reaction 6). Ledwith and coworkers[12] showed that quantum yields for formation of propagating cations fall steadily as

reaction proceeds due to the very rapid chain induced decomposition of iodonium salt and relatively low consumption of DMPA. Furthermore, the rate of polymerization was affected by both photoinitiator DMPA and the iodonium salt as measured dilatometrically[13]. Figure 1 shows that in the polymerization of THF, the rate of polymerization approached a limiting value upon increasing the iodonium salt concentration. Presumably, iodobenzene, produced in the system, attacks propagating cations to form an iodonium salt, e.g.:
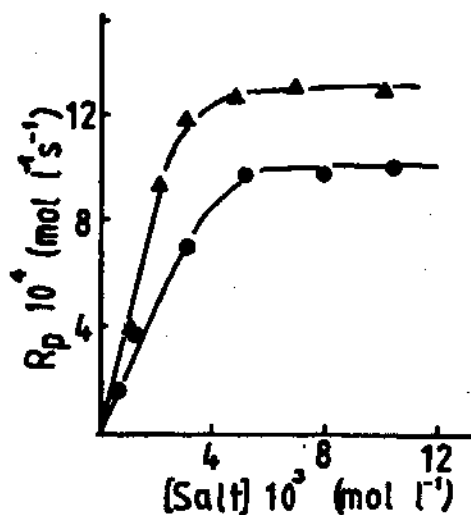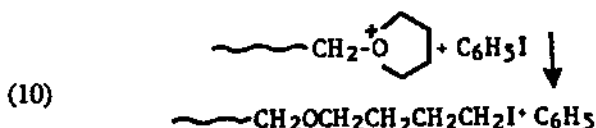
(10) $$----CH_2-\overset{+}{O}\bigcirc + C_6H_5I \downarrow$$
$$----CH_2OCH_2CH_2CH_2I^+ C_6H_5$$

Figure 1. Dependence of rate of polymerization of THF (bulk) on $(p-CH_3C_6H_4)_2I^+PF_6-$ at $(\bullet)$DMPA $= 5 \times 10^{-3}$ M and $(\triangle)$ DMPA $= 10^{-2}$M at 25°C, $\lambda = 366$ nm.

Similarly, Pappas, et al.[5] confirmed a high nucleophilic reactivity of iodobenzene towards the transient PhI^+ with $k=7.5 \times 10^7$ l mol^{-1}s^{-1}, which may also result in the formation of a new iodonium salt. Support for termination of iodobenzene was readily obtained by studies of polymerization of THF initiated independently of the iodonium salt. For example, there is an appreciable reduction in conversion when polymerization of THF is initiated thermally by p-chlorophenyldiazonium hexafluorophosphate in the presence of iodobenzene (Table 1). Similarly, the rate of polymeriza-

tion increased with DMPA until a certain concentration was reached, and thereafter leveled off, probably owing to complete light absorption by the free radical source (Figure 2). The same behavior was observed when benzophenone was employed. Benzophenone is known to undergo photoinduced hydrogen abstraction reaction with THF and cation formation would then follow as shown below.

In this case, benzophenone would be regenerated by means of the electron transfer reaction of Ph_2C-OH radical. G.l.c. product analysis confirmed that there was no loss of benzophenone after irradiating bulk THF containing 10^{-2} M benzophenone and 5×10^{-3} M p-chlorophenyldiazonium hexaflourophosphate for 45 minutes at 366 nm.

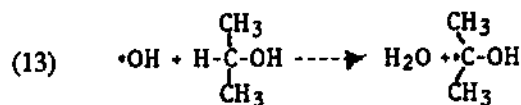| Bulk polymerization[13] of THF Initiated by p-ClC6H4N2+PF6-(5×10^{-3}M) at 95° C. Initiation time, 5 min; Subsequent Polymerization at 25° C for 90 min.	
Iodobenzene	Conversion
(M)	(%)
0	6
2×10^{-3}	2.5
10^{-2}	2.1
2×10^{-2}	1.9

Pulse Radiolysis Studies[14]

Occurrence of the process described above was further substantiated by the independent generation of diphenliodo radicals in the absence of potential overlapping choromophores such as benzophenone ketyl radical. For this purpose, dilute aqueous solutions of $Ph_2I^+PF_6^-$ were irradiated with single pules of 17 Mev electrons. The solutions were saturated with N_2O prior to irradiation in order to convert hydrated electronics to OH radicals according to reaction 12.

$$(12) \quad e^- + N_2O \longrightarrow \cdot OH + OH^- + N_2$$

The hydroxy radicals were permitted to react almost totally with 2-propanol contained in the system at a concentration of 1.1 M. In this way 2-hydroxy-2-propyl radicals were formed.

Figure 2. Dependence of rate of polymerization of THF(bulk) on DMPA at $(p\text{-}CH_3C_6H_4)_2I^+PF_6^- = 5 \times 10^{-3}$M at 25° C, $\lambda = 366$nm.

$$(13) \quad \cdot OH + H\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}OH \longrightarrow H_2O + \cdot\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}OH$$

Reaction 13 occurs very rapidly with $k=4 \times 10^9$ $1mol^{-1}s^{-1}$. When a 50 ns electron pulse was applied to the solution, the transient absorption spectrum shown in Figure 3 with a maximum at about 390 nm was formed. This spectrum is attributed to the iodo radical according to reaction 14.
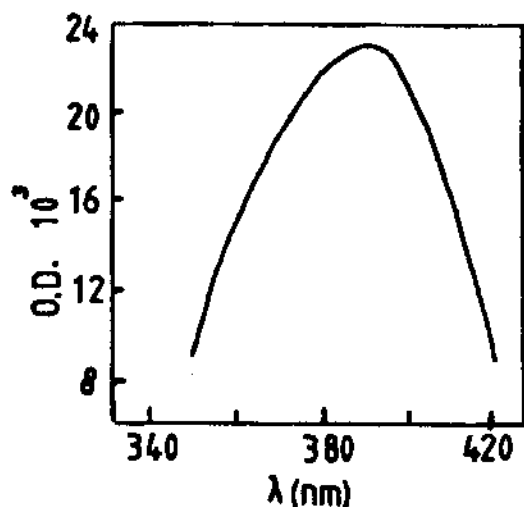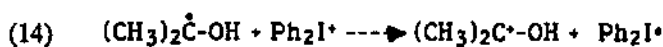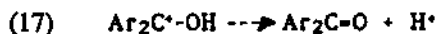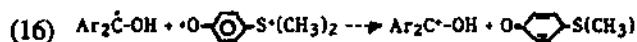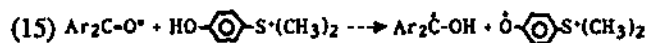
(11)

Figure 3. Irradiation of an N₂O-saturated aqueous solution containing Ph₂I⁺PF₆⁻(4 x 10⁻³ M) and 2-propanol (1.12 M). The spectrum presented here was obtained from the difference in the optical densities recorded at 10 and 1µs after the end of the pulse. Dabs = 60 Gy.

(14) $(CH_3)_2\dot{C}\text{-OH} + Ph_2I^+ \dashrightarrow (CH_3)_2C^+\text{-OH} + Ph_2I\cdot$

By this finding, the occurrence of the electron transfer process between iodonium salt and electron donor radicals was further substantiated. The rate constant of the reaction of 2-hydroxy-2-propyl radicals was determined as 6×10^7 1 mol⁻¹s⁻¹. Bauman, et al.[15] reported a similar value (3×10^7 1 mol⁻¹ s⁻¹) for the rate constant of the reaction of benzophenone ketyl radical (Ph₂C-OH) with Ph₂I⁺ ions. The slightly higher value found in our case is probably due to higher electron density at the radical site in the 2-hydroxy-2-propyl radical.

It is interesting to note that 2-hydroxy-2-propyl radicals did not react with Ph₃S⁺ ions. These findings are in accordance with the fact that Ph₃S⁺ ions are not capable of initiating the free radical promoted cationic polymerization. In this connection, the behavior of dialkyl (4-hydroxyphenyl) sulphonium salts (DHPS)[16] and 4- (phenylthio) phenyldiphenyl sulphonium salts (PTPDS)[12] is notable. Photosensitization of DHPS by aromatic ketones such as benzophenone involved H abstraction from the phenol group followed by electron transfer between the resulting ketyl radical and phenol radical cation.

(15) $Ar_2C\text{-O}\cdot + HO\text{-}⟨O⟩\text{-}S^+(CH_3)_2 \dashrightarrow Ar_2\dot{C}\text{-OH} + \dot{O}\text{-}⟨O⟩\text{-}S^+(CH_3)_2$

(16) $Ar_2\dot{C}\text{-OH} + \cdot O\text{-}⟨O⟩\text{-}S^+(CH_3)_2 \dashrightarrow Ar_2C^+\text{-OH} + O\text{=}⟨⟩\text{=}S(CH_3)$

(17) $Ar_2C^+\text{-OH} \dashrightarrow Ar_2C\text{=}O + H^+$

In these reactions the sulphonium salt functions both as H donor and electron acceptor. Similarly, an accelerating influence of added free radical source DMPA was observed[12] when polymerization of THF was photoinitiated by PTPDS upon irradiation at 350 nm from a Rayonet Merry-go-Round photoreactor. Although both PTPDS and DMPA absorbed the light, this result led to the conclusion that a radical promoted cationic initiation mechanism became operative in this case. It seems likely that electron transfer between photogenerated diphenylsulphide cation radical and dimethoxy phenyl methyl radical may occur.

(18) $Ph\text{-}\underset{OCH_3}{\overset{OCH_3}{C}}\cdot + Ph_2I^+ \dashrightarrow Ph\text{-}\underset{OCH_3}{\overset{OCH_3}{C^+}} + Ph_2I\cdot$
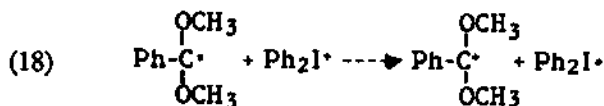
Acylphosphine Oxides as Radical Promoters[17]

The capability of acylphosphine oxides, such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMPDO) to promote the cationic polymerization of appropriate monomers was recently examined[17]. TMPDO undergoes α-cleavage with a quantum yield of ca 0.6[18].

(19)
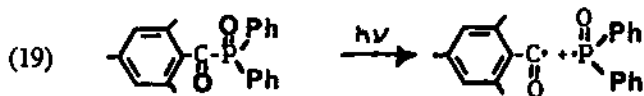
Laser flash photolysis revealed that phosphorus-centered radicals were not oxidized by iondonium ions: when TMDPO was irradiated in dichloromethane solution with 20 ns. flash of 347 nm light, both the extent of the optical density due to diphenylphosphonyl radical (Ph₂P=0) build up during the flash and the rate of decay of the optical density were not
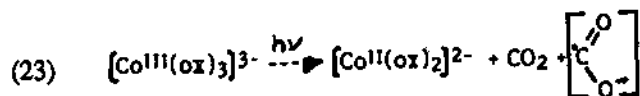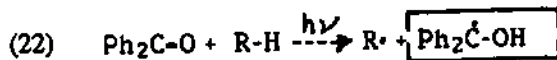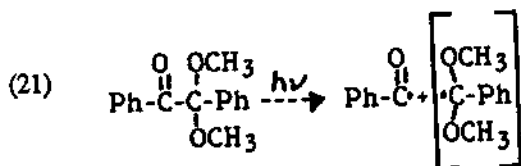
influenced by $Ph_2I^+PF_6$- present in the solution. Thus, it was concluded that $Ph_2P=O$ does not react with Ph_2I^+ ($k<10^6$ 1 mol^{-1} s^{-1}). However, THF was readily polymerized upon irradiating it in the presence of TMDPO and $Ph_2I^+PF_6$- at 379 nm, where only TMDPO absorbs light. Recent studies[19] revealed that chain-initiating cations were formed by hydrogen abstraction of trimethyl benzoyl radicals (reaction 20) followed by electron transfer (reaction 8).

(20)
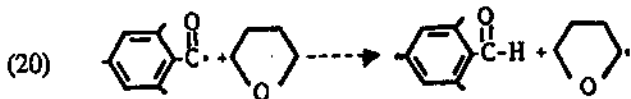
Thus, trimethylbenzoyl radicals contribute indirectly to the formation of carbocations. Apart from THF, butyl vinylether (BVE) also underwent cationic polymerization when irradiated with 366 nm light in the presence of TMDPO and $Ph_2I^+PF_6$-. It appeared that, in this case, $Ph_2P=O$ radicals added to the C-C double bond thus giving rise to the formation of carbon centered radicals of high reactivity towards Ph_2I^+ ions. It is notable that $Ph_2P=O$ radical is of relatively high reactivity towards BVE[20] ($k_{R+BVE}=4\times10^6$ 1 mol^{-1} s^{-1}).

## Electron Transfer Process in Free Radical Polymerizing Systems

As mentioned in the introduction, most of technically applied photochemical curing processes are based on free radical polymerization and usage of free radical initiators. The chemical structure of the photoinitiators contributes to the spectral sensitivity and efficiency of the photogenerated radicals. Upon irradiation, some photoinitiators yield nucleophilic radicals which do not efficiently add to the double bonds. Several examples[8], of light induced formation of nucleophilic radicals are shown below.

(21) $Ph-\overset{O}{\overset{||}{C}}-\overset{OCH_3}{\underset{OCH_3}{\overset{|}{C}}}-Ph \xrightarrow{h\nu} Ph-\overset{O}{\overset{||}{C}}\cdot + \left[\cdot\overset{OCH_3}{\underset{OCH_3}{\overset{|}{C}}}-Ph \right]$

(22) $Ph_2C=O + R-H \xrightarrow{h\nu} R\cdot + \boxed{Ph_2\overset{.}{C}-OH}$

(23) $[Co^{III}(ox)_3]^{3-} \xrightarrow{h\nu} [Co^{II}(ox)_2]^{2-} + CO_2 + \left[\overset{O}{\underset{O}{\overset{}{C}}} \right]$

It was shown by Timpe and coworkers[21] that the rate of photopolymerization of monomers such as methylmethacrylate (MMA) and acrylamide (AA) initiated by nucleophilic radical precursors increases when onium salts were added. The main effect on photopolymerization rate is caused by oxidation of the inhibiting nucleophilic radicals by onium salts to give reactive arene radicals which initiate vinyl polymerization according to reactions 24 and 25.

(24) $\cdot R_{nu}^{\cdot} + Ph_2I^+ \dashrightarrow R_{nu}^{+} + Ph\cdot + PhI$

(25) $Ph\cdot + M \dashrightarrow polymer$
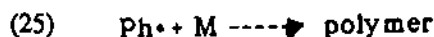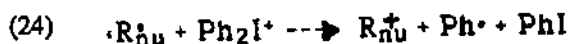
Similarly, the use of phenylazotriphenylmethane (PAT) as a free radical initiator is restricted by its property to terminate growing chains. The azo compound may be decomposed thermally and photochemically to give a triphenylmethyl radical and a phenyl radical.

(26) $Ph_2C=O + R-H \xrightarrow{h\nu} R\cdot + \boxed{Ph_2\overset{.}{C}-OH}$
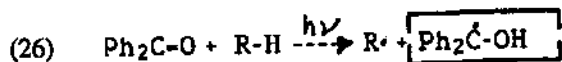
Triphenylmethyl radical is a relatively stable free radical and functions only as a chain initiator at low concentrations. With large quantities of triphenylmethyl radicals chain growth is restricted and low molecular weight polymers are obtained with vinyl type monomers. In our laboratory, we have shown[22] that the use of diphenyl iodonium salt converts terminating triphenylmethyl radicals to the corresponding cations and thus improves the efficiency of PAT as a free radical initiator. Data for a series of polymerization of MMA initiated by PAT in the absence and presence of diphenyliodonium salt as an oxidizing salt are presented in Table 2. A further extension[5] of the concept of free radical promoted cationic polymerization is the design of photocurable systems which contain photoinitiators and functionality

for both radical and cationic polymerization. It appears that hybrid systems may provide enhanced light utilization and more efficient utilization of reactive intermediates.

Possibilities for Preparing Block Copolymers by Electron Transfer Process

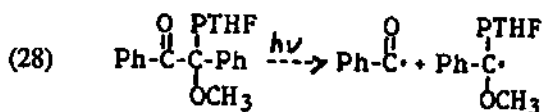DMPA was shown[13] to be an efficient transfer agent in the cationic polymerization of THF. The transfer constant was estimated to be 2.8. The high reactivity of DMPA in chain transfer to living polytetrahydrofuran (PTHF) chains having photochemically active end groups may be understood according to the following reactions.

(27)

$$\sim O^{+}\bigcirc + Ph-\overset{O}{\underset{\parallel}{C}}-\overset{OCH_3}{\underset{OCH_3}{\overset{\mid}{C}}}-Ph$$

$$\downarrow$$

$$Ph-\overset{O}{\underset{\parallel}{C}}-\overset{CH_3}{\underset{OCH_3}{\overset{O^{+}}{\underset{\mid}{C}}}}-Ph \quad \overset{CH_2CH_2CH_2CH_2O\sim}{}$$

$$\downarrow$$

$$Ph-\overset{O}{\underset{\parallel}{C}}-\overset{\cdot}{\underset{OCH_3}{\overset{\mid}{C}}}-Ph \quad + \quad CH_3OCH_2CH_2CH_2CH_2O\sim$$

$$\downarrow \quad \bigcirc_{O}$$

$$Ph-\overset{O}{\underset{\parallel}{C}}-\overset{OCH_2CH_2CH_2CH_2-O^{+}\bigcirc}{\underset{OCH_3}{\overset{\mid}{C}}}$$
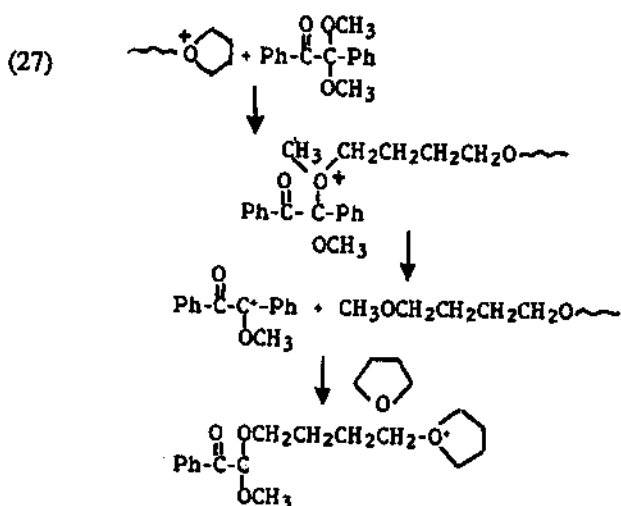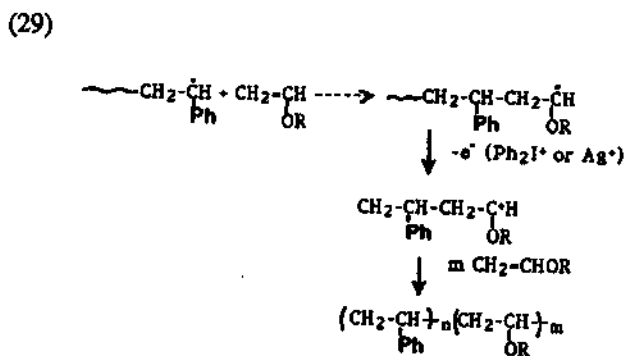
This process leads to polymers with 2,2-dialkoxy acetophenone end groups. PTHF functionalized in this way will decompose on photolysis and form two radicals similar to DMPA.

(28)

$$Ph-\overset{O}{\underset{\parallel}{C}}-\overset{PTHF}{\underset{OCH_3}{\overset{\mid}{C}}}-Ph \quad \overset{h\nu}{\dashrightarrow} \quad Ph-\overset{O}{\underset{\parallel}{C}}\cdot \quad + \quad Ph-\overset{PTHF}{\underset{OCH_3}{\overset{\mid}{C}}}\cdot$$

If the photolysis is carried out in the presence of free radical polymerizable monomers such as styrene (St) and MMA, the PTHF attached radical may initiate free radical polymerization to generate copolymers. Preliminary experiments concerning polymerization of St and MMA by means of photochemically active PTHF showed that, while initiation was efficiently achieved, homopolymer formed to an appreciable extent. This is to be expected since the PhCO radical is capable of initiating polymerization of added monomer, thereby generating homopolymer simultaneously with PTHF copolymers. Unfunctionalized PTHF present in the initial polymer is an additional reason for the presence of homopolymer. Alternatively, oxidation of electron donor macroradicals induces cationic polymerization and this procedure enables block copolymers to be produced, since the free radical possesses polymeric segments. For this purpose, the free radical promoted cationic polymerization of BVE was achieved[23] by thermal decomposition of active PSt having peroxy-linkage in the presence of Ph_2I^{+} and Ag^{+} ions.

(29)

$$\sim CH_2-\overset{\cdot}{\underset{Ph}{C}}H + CH_2-\overset{\cdot}{\underset{OR}{C}}H \dashrightarrow \sim CH_2-\overset{\cdot}{\underset{Ph}{C}}H-CH_2-\overset{\cdot}{\underset{OR}{C}}H$$

$$\downarrow -e^{-} (Ph_2I^{+} \text{ or } Ag^{+})$$

$$CH_2-\overset{\cdot}{\underset{Ph}{C}}H-CH_2-\overset{+}{\underset{OR}{C}}H$$

$$\downarrow m \ CH_2=CHOR$$

$$(CH_2-\overset{\cdot}{\underset{Ph}{C}}H)_n(CH_2-\overset{\cdot}{\underset{OR}{C}}H)_m$$

It should be pointed out that silver salt is more suitable due to the fact that it acts as a one-electron oxidant and initiation of growing chains is not multiplied by regeneration of phenyl radicals from the reduction of the iodonium salt. However, polymer samples obtained by this procedure contained only a very small fraction of block copolymer structure due to the phase separation and very effective chain transfer reactions predominating the cationic polymerization of BVE. The attachment of dibenzazepine derivatives to polymer chains as terminal units is a convenient procedure for chain extension or block copolymer formation by photo-induced cylodimerization.

(30)
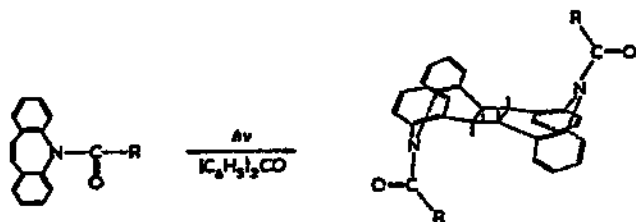
Structurally related specific groups may be attached to the ends of polymer chains in several ways[24-27]. More recently we have used[24] radical promoted cationic polymerization to prepare PBVE with N-acyl dibenzazepine terminal units (reactions 31) which may participate in block copolymer formation according to reaction 30.

(31)
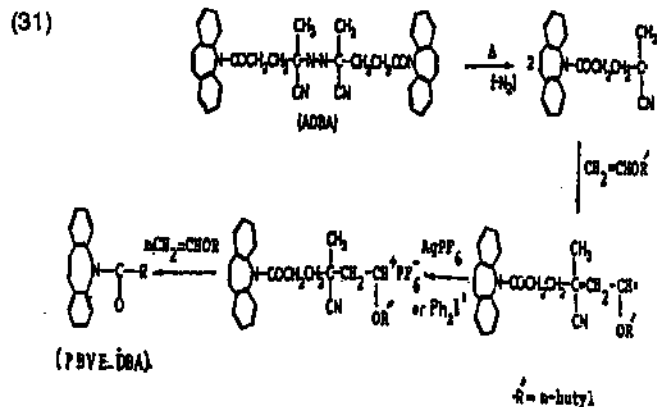
As described previously, the method is based on the diversion of alkoxy alkyl radicals to the corresponding carbocations with the aid of organic salts. Polymer samples prepared in the presence of $AgPF_6$ contained a significant number of terminal dibenzazepine units, while in the presence of iodonium salt containing only a very small fraction of macromolecules having these photosensitive groups.

The author wishes to acknowledge his collaboration with Professors Anthony Ledwith, S. Peter Pappas, and Wolfram Schnabel, and partial financial support from Alexander-von-Humboldt Stiftung.

References

1. UV Curing: Science & Technology, ed. S. P. Pappas, Technology Marketing Corp., Norwalk, CT, 1978; Vol. II, 1985.

2. J. V. Crivello in "Developments in Polymer Photochemistry," ed. N. S. Allen, Applied Sci. Publishers, 1981, pp.1-39.

3. J. V. Crivello in "UV Curing: Science & Technology," pp. 23-77.

4. J.V. Crivello and J. H. Lam, Macromolecules 10, 1307 (1977).

5. S. P. Pappas, B. C. Pappas, L. R. Gatechair, and W. Schnabel, J. Polym. Sci., Polym. Chem. , Ed. 22, 69 (1984).

6. V. D. McGinniss in "UV Curing:Science & Technology," pp. 97-133.

7. A. Ledwith, Polymer, 19, 1217 (1978); F. A. M. Abdul-Rasoul, A. Ledwith and Y. Yagci, 191, 1219 (1978).

8. S. P. Pappas, B. C. Pappas, L. R. Gatechair, J. H. Jilek and W. Schnabel, Polym. Photochem., 5,1 (1984).

9. H. J. Timpe, Sitzungberichte der Akademie der Wissenshaften der DDR, 13 N, Akademie Verlag, Berlin, 1986.

10. S. P. Pappas, L. R. Gatechair, and J. H. Jilek, J. Polym. Sci., Polym. Chem., Ed. 22,77 (1984).

11 Y. Yagci, Ph.D. Thesis, University of Liverpool, Liverpool, UK, 1979.

12. A. Ledwith, S. Al-Kass and A. Hulme Lowe in "Cationic Polymerization and Related Processes," ed. E. J. Goethal, Academic, New York, 1984, p. 278.

13. Y. Yagci and A. Ledwith, J. Polym. Sci., Polym. Chem. Ed., 26, 1911 (1988).

14. Y. Yagci, S. P. Pappas and W. Schnabel, N. Naturforch., 42a, 1425 (1987).

15. H. Baumann and H. J. Timpe, Z. Chem., 23,394 (1983).

16. J. V. Crivello, Adv. Polym. Sci., 62,1 (1984).

17. Y. Yagci and W. Schnabel, Makromol. Chem., Rapid Commun., 8,209 (1987).

18. T. Sumiyoshi, W. Schnabel, A. Henne and P. Lechtken, Polymer 26,141 (1985).

19. Y. Yagci, J. Borbely and W. Schnabel, Eur. Polym. J., in press.

20. T. Sumiyoshi and W. Schnabel, Makromol. Chem., 1861811 (1985).

21. H. Baumann and H. J. Timpe, Act. Polym., 37,309 (1986).

22. Y. Yagci, A. E. Sizgek and A. C. Aydogan, J. Poly. Sci., Polym Let. to Ed., 22,103 (1984).

23. Y. Yagci, M. Acar, G. Hizal, H. Yildirim, and B. Baysal, Angew. Macromol. Chem., 154,169 (1987).

24. Y. Yagci, W. Schnabel and A Ledwith, Eur. Polym. J., 23,737 (1987).

25. A. K. Alimoglu, C. H. Bamford, A. Ledwith and S. U. Mullik, Macromolecules, 10,1081 (1977).

26. C. H. Bamford, A. Ledwith, and Y. Yagci, Polymer, 19,354 (1978).

27. A. K. Alimoglu, Ph.D. Thesis, University of Liverpool, Liverpool, UK, 1979.

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