Radiation Curing of Collagen/Divinyl Ether Enhanced by Pyridinium Salts

Bo Jiang,[1] Yong Zhou,[2] Zheng Yang,[3] Zhihong Wu,[1] Guanglin Huang,[4] Libin Lin,[2] Xingdong Zhang[1]

[1]*Engineering Research Center for Biomaterials, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China*
[2]*Key Laboratory for Radiation Physics and Technology of Education Ministry, Institute of Nuclear Science and Technology, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China*
[3]*Analytical and Testing Center, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China*
[4]*Department of Chemistry, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China*

ABSTRACT: The radiation curings of collagen/divinyl ether enhanced by several nitrogenous onium salts having relatively stable nonnucleophilic anion (PF_6^-) have been investigated. Results of glass transformation temperature (T_g) measurements and IR spectroscopy analysis and solvent extractions to the crosslinked polymer networks demonstrate that the curing reactions have been initiated by electron beam irradiation in the mixture system of collagen/divinyl ether and onium salts under different atmosphere conditions. The experimental data show the presence of an approximating linear relationship between double bond conversion and gel fraction after the calculation of conversion from IR spectra in oligomer and the measure of gel content at different total radiation doses. Practical values approximate theoretical values in applying gelation theory of the relationship of gel fraction and double bond conversion. In comparison with the influence of different inhibitors, the curing reaction with pyridinium salts is a polymerization and crosslinking of cationic mechanism, but radicals play an important role in initiation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2094–2100, 2005

Key words: electron beam; radiation curing; onium salts; divinyl ether; collagen

INTRODUCTION

In bone tissue engineering, a highly porous artificial extracellular matrix or scaffold is essential to the attachment, proliferation, and differentiation of bone cell and the formation of bone tissue. However, conventional scaffold materials for bone tissue engineering proved less valuable for actual applications because they lack mechanical strength, interconnected channel network, and controllable porosity or channel size. Therefore, exploration of the ideal scaffold materials is one of the popular studies on current bone tissue engineering. The application and advancement of a newly developed technology is generally know as rapid prototyping techniques in bone tissue engineering. High-energy electron beam (EB) is also a direct, effective, attractive energy source for radiation curing of the porous superposition film materials in comparison with other initiating means. Obviously, the complicated polymer network, so much as interpenetrating polymer network, of curings of collagen blended with triethylene glycol divinyl ether serves not only to increase mechanical strength of cured porous scaffold materials but also to provide activating vinyl ether groups for radiation curing.

In recent years the development of electron beam radiation curing for the rapid, pollution-free, low-energy polymerization and crosslinking of multifunctional monomers and oligomers for coating and composite applications has become an established technique. The uses of various ionizing radiations to induce free radical polymerizations are well known. In comparison with UV light utilized widely as a radiation source, the reason that electron beam curing of radical mechanism is less used is that coatings or composites cannot be fully cured owing to the inhibitive oxygen effect. So-called "free cationic" polymerizations are observed only when scrupulously dry, oxygen-free, and ultra pure monomers are used. Thus, they are not suitable for practical applications in bone tissue engineering.

Many studies on photo-induced cationic polymerization have been published as the foundational research of cationic mechanism curing in recent years.[1–10] Some iodoniums and sulfoniums irradiated with UV light were discovered not only to get Bronsted acids by direct photodecomposition but also to obtain carbenium via an electron transfer process to

initiate cationic polymerization. This is because the many onium salts with a relative higher reduction potential can oxidize the α-free radical of vinyl ethers and epoxides with a lower oxidation potential. The different free radical sources, such as α-radicals of vinyl ethers and epoxides, have been generated thermally, photochemically, and ionizing-radiatively.[1,4,11,12] In most of the earlier studies on ionizing radiation-induced cationic polymerization enhanced by various onium salts, the monomer and the onium salt are all dissolved in a polar or nonpolar solvent, and the experiments are carried out at very low temperature. Obviously, solvent effect is important to the cationic polymerization. It is difficult to elucidate that there may be other influences to produce a charge transfer complex among monomers, onium salt, and solvents. However, the curing system of coating and composites consists mainly of oligomers and multifunctionic monomers, which have almost no solvents, in fact. The onium salts themselves must be dissolved in multifunctionic oligomer and active dilutes in the system at room temperature. With rapid prototyping techniques application and bone tissue engineering development, known onium salts, such as iodoniums and sulfoniums, cannot fully be satisfied owing to the cytotoxicity of leftovers that are removed with difficulty. The studies of reactive mechanisms have focused on the oxidation of free radicals in center carbon by various onium salts in solvent-free systems and different free radical sources.[9,13,14] Based on above reason, this paper describes a study of radiation curing of collagen/divinyl ether in the presence of several nitrogenous onium salts induced by electron beam and assesses the radiation effect and curing reactive mechanism.

METHODS

Materials

Triethylene glycol divinyl ether (DVE-3)

DVE-3, which was purchased from ISP, was distilled at reduced pressure after being dried with calcium hydride (CaH_2).

Fabrications of reconstituted collagen and blend with DVE-3

Calfskin was cleaned, comminuted, washed in cold aqueous sodium chloride, and swollen in $0.5M$ acetic acid. It was digested for several days with pepsin, and the digest was centrifuged to remove undigested skin. Purification of the solubilized collagen was accomplished by sodium chloride fractionation and fibril assembly. Then, dry collagen was dissolved into DVE-3 solution with onium salt.
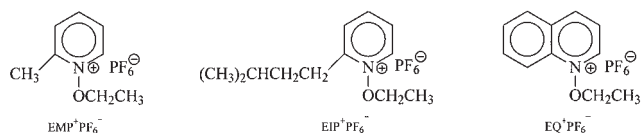
Scheme 1

N-Ethoxy-2-methypyridinium hexafluorophosphate ($EMP^+PF_6^-$)

$EMP^+PF_6^-$ was prepared according to a procedure described by Reichardt.[15] It was recrystallized from ethanol.

N-Ethoxy-2-isopentylpyridinium hexafluorophosphate ($EIP^+PF_6^-$)

$EIP^+PF_6^-$ was synthesized in our laboratory. The yield was 8.1 g or 80.2%. For $C_{12}H_{20}NOPF_6$ (molecule weight is 339.09), element analysis: C, 42.50%; H, 5.90%; N, 4.13%; found: C, 42.51%; H, 5.94%; N, 4.15%; m/z: 194, 166, 149. The infrared (IR) spectrum (KBr) shows at v_{N-O} 1264 and v_{C-O} 1060 cm^{-1}.

N-Ethoxypyridinium hexafluorophosphate ($EQ^+PF_6^-$)

$EQ^+PF_6^-$ was synthesized in our laboratory. The yield was 9.1 g or 64%. For $C_9H_{12}NOPF_6$ (molecules weight is 260.8), element analysis: C, 41.41%; H, 4.60%; N, 5.37%; found: C, 41.69%; H, 4.77%; N, 5.25%; m/z: 174, 145, 129. The IR spectrum (KBr) shows at v_{N-O} 1268 and v_{C-O} 1083 cm^{-1} (Scheme 1).

EB irradiation

Appropriate proportional mixtures of DVE-3 and collagen, which contained a given amount of onium salts, were placed in shallow glass container. The mixtures in the shallow glass container were degassed in the degasser and then filled with dry air, nitrogen, or oxygen at low temperature. Shallow containers of the different atmosphere conditions were obtained after being sealed off with polyethylene film. The samples were irradiated by electron beam from an electron accelerator of 300 KeV at controlled temperatures.

The absorptive dose equation of accelerator is expressed as

$$D = \frac{F(R)EI}{LVS\rho} \times 10^3,$$

where D is absorptive doses in Gy, E is electron energy in MeV, I is electron beam current in μA, L and ρ are, respectively, thickness (in cm) and density (in g cm^{-3}) of coating membranes and V and S are, respectively, rate (cm s^{-1}) and width (cm) of electron beam scan-

ning. *F(R)*, which is the characteristic absorptive coefficient, is obtained from

$$R = \frac{\rho P N_0}{E} \sum f_i (Z/A)_i.$$

Z, *A*, and N_0 are, respectively, atomic number, atomic weight, and Avogadro's constant. Looking up the *F(R)~R* curve will give the characteristic absorptive coefficient value after *R* value is calculated.

Characterization

Pretreatment

The irradiated samples were extracted to constant weight by benzene for obtaining gel materials and calculated gel fraction in different irradiation doses.

Differential scanning calorimetry (DSC)

DSC measurements ware performed using a Perkin-Elmer DSC7 m. The operational conditions were air atmosphere and rising temperature rate 10 °C.min^{-1}.

IR spectrum

IR spectrum measurements ware recorded by a Nicolet 20SXB FTIR spectrophotometer. The coating membranes were directly measured after the glass coated by liquid samples was irradiated by electron beam, and the coating membrane was peeled off from the glass.

RESULTS AND DISCUSSION

Different from polymerizations of typical monomers, multifunctional compounds, such as triethylene glycol divinyl ether (DVE-3) and the like, are both active
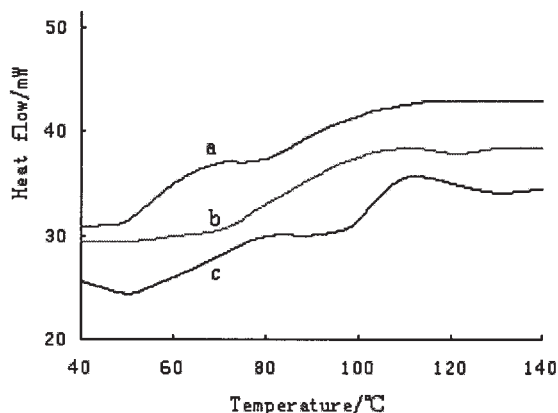

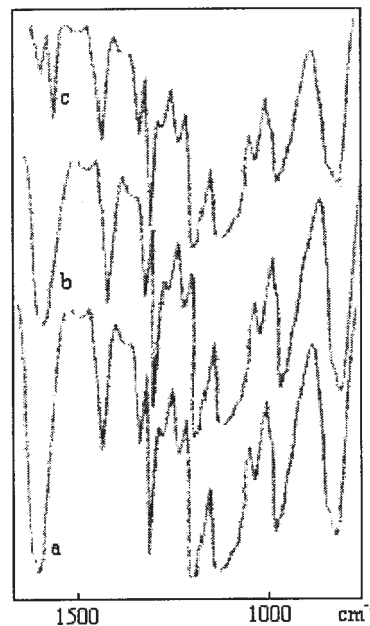**Figure 1** DSC spectra: (a) misture of p(DVE-3) and collagen, (b) p(DVE-3), and (c) collagen.

Figure 2 FTIR spectrum. Radiation doses: (a) 0 KGy, (b) 10 KGy, and (c) 25 KGy.

diluents and main reactive oligomers in the radiation curing reaction. The vinyl ether compounds can be rapidly polymerized without protonic impurities, usually achieved by rigorous drying techniques under high vacuum, when irradiated by the high-energy ray to give a solid polymer. This phenomenon occurs because cationic polymerization is initiated by the free cations in the absence of anti-ion, which is highly sensitive to any basic impurities in polymerization. However, a most viscous substance is only obtained after triethylene glycol divinyl ether (DVE-3) or a mixture of the divinyl ether with collagen irradiated by electron beam in air. If the DVE-3 or the mixture in the presence of *N*-ethoxy-2-methypyridinium hexafluorophosphate ($EMP^+PF_6^-$) of nitrogenous oniums ranging from 0.1 to 0.3% is irradiated by the electron beam of 300 keV, solid polymers of the membrane state will be obtained in dry air. The two glass transformation temperatures (T_g), which are, respectively, 65 and 96 °C, were discovered by the thermal analysis method. Compared with curves b and c in Figure 1, the glass transformation temperature of curve a is cognized for 96 °C, which is from poly(triethylene glycol divinyl ether). This also indicates that divinyl ether is a pivotal component in the curing system, and collagen in the complicated polymer network has only been crosslinked. Therefore, the relationship of divinyl ether with nitrogenous oniums irradiated by electron beam is a key question of radiation curing of collagen/divinyl ether enhanced by pyridinium salts.

IR spectra of poly(triethylene glycol divinyl ether) in different irradiation doses are shown in Figure 2. The characteristic absorptive band at 1641 and 1617

TABLE I
The Relationship of Onium Salts and Gel Fraction

Onium salt	Atmosphere conditions	3 K Gy	30 K Gy
$EMP^+PF_6^-$	Dry air	0.18	0.72
$EIP^+PF_6^-$	Dry air	0.20	0.71
$EIP^+PF_6^-$	Oxygen	0.18	0.73
$EIP^+PF_6^-$	Nitrogen	0.24	0.80
$EQ^+PF_6^-$	Dry air	0.25	0.85

Note. The concentrations of onium salts are 0.3% at 25°C.

cm^{-1} comes from Fermi resonance of the alkene bond $V_{C = C}$ and the multifrequency of absorptive band at 810 cm^{-1} in spectral line a in the Figure 2. Comparing absorptive intensity with of the spectral bond at 1087 cm^{-1}, which is absorption of stretching vibration of ether bond, the characteristic absorptive bands at 1641 and 1617 cm^{-1} of the double bond is reduced with increasing irradiation doses. Obviously, the falling intensity of the characteristic peak in the IR spectra means that the quantity of double bonds in vinyl ether decreases continuously with the carrying out of the curing reaction.

Gel fraction measurements can afford more useful information. Influences of several onium salts to gel fraction of poly(triethylene glycol divinyl ether) under different atmosphere conditions are shown in Table I. Since onium salts $EIP^+PF_6^-$ and $EQ^+PF_6^-$ have better compatibility in DVE-3 than onium salt $EMP^+PF_6^-$, the gel fraction value is rather bigger under different atmosphere conditions. Although the largest yield rates of gel are obtained in the presence of onium salt $EQ^+PF_6^-$ as shown in Table I, the product has quite a dark color, and onium salt $EQ^+PF_6^-$ itself is not very stable. Compared with experimental data in the presence of onium salt EIP^+PF_6 in Table I, they show approximate gel fraction values under different atmosphere conditions such as nitrogen, dry air, and oxygen.

For studying the relationship of gel and sol of poly-(triethylene glycol divinyl ether), the irradiated samples are extracted to constant weight by benzene for obtaining gel and sol materials and calculated gel fraction in different irradiation doses. The relationship of radiation doses and gel fraction and sol fraction is illustrated in Figure 3. Because the initial rates of polymerization and/or crosslinking are rapid, the gel fraction curve heightens swiftly. When the sol fraction curve gently changes slope after 20 KGy, the polymerization rates might have decreased, but the crosslinking reactions are still continuously carrying through in the system. The experimental results prove that the crosslinking gel web can be obtained even if the mixture of DVE-3 and nitrogenous oniums is irradiated in relatively fewer dose conditions, for example, 3.5 KGy in Figure 3. Therefore, the curing reaction in the presence of pyridinium salts obviously not only elevates

the polymerization rate similar to polymerization in solution,[7] but also increases simultaneously the polymerization and crosslinking rates in the system with mutilfunctional oligomers. And similar to radiation crosslinkage of the usual polymer, the curing reaction of triethylene glycol divinyl ether likewise submits to the general rule even if there are nitrogenous onium salts in a reactive system. Although the radiation curing reaction of divinyl ether might have various reactive mechanisms, the above experimental data indicate that the important influence of the pyridinium salts in this curing system cannot be ignored The fact of obtaining dry solid polymer materials means that the curing of divinyl ether is enhanced by several onium salts under ionizing radiation. The curing in the presence of onium salts, which is not influenced by oxygen, might have a complex mechanism different from general free radical or cationic polymerizations.

The absorptive band at 1087 cm^{-1} of the ether bond, owing to there being no chemical reactions, is selected as a relative inner standard for eliminating error difference from the thickness of coating membranes in Figure 2. The height of the absorption peak is measured from the IR spectra at different total irradiation doses. The double bond conversion can be characterized with the height reduction of the absorptive band at 1641 cm^{-1}, which is approximately equal to the $P_C = C$ value calculated from the equation of $P_{C = C}$ versus gel fraction. The double bond conversion at 1641 cm^{-1} is calculated as

$$P_{C=C} = 1 - \left(\frac{A_{1641}/A_{1087}}{A'_{1641}/A'_{1087}}\right).$$

Figure 4 describes an approximating linear relationship of double bond conversion and the gel fraction when the gel fraction is less than 0.6. Extrapolating line stretches right to the Y axis to obtain the gelation point value for 0.35 in the reactive system. Obviously,
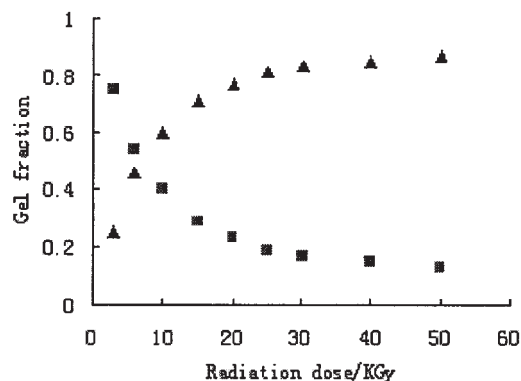

Figure 3 Relationship of radiation doses and gel fraction. (▲) Gel fraction; (■) sol fraction. 0.3% $EMP^+PF_6^-$ and dry air saturated at 25 °C.
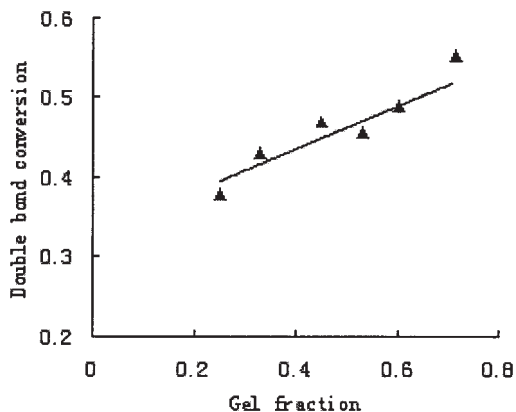
Figure 4 Relationship of gel fraction and double bond conversion. 0.3% $EMP^+PF_6^-$ and dry air saturated at 25 °C.

Figure 6 Relationship of gel fraction and double bond conversion in the whole system. (●) Theoretical value; (▲) practical value. 0.3% $EIP^+PF_6^-$ and dry air saturated at 25 °C.

the experimental conclusion approaches equal one-third the value of double bond conversion in gelation theory.

The theoretical and practical values are compared in Figures 5 and 6 for discussing the influence of onium salts on the curing reaction and the distribution of sol and gel after the gelation point. There is a distributed process of sol decreasing and gel increasing after the gelation point, as shown in Figures 5 and 6. The calculated methods of the theoretical values are from the literature.[16] According to the literature, the less theoretical values are here due to no consideration of the inner circular reaction in the theoretical calculative equation. Practical value approximating theoretical value is shown in Figures 5 and 6. The gelation point and the distributive level of sol and gel in the reactive system have no change after nitrogenous onium salts are added to the curing. Therefore, the above-mentioned data demonstrate that the gel point and the gel distribution rule are not influenced by the presence of nitrogenous onium salts.
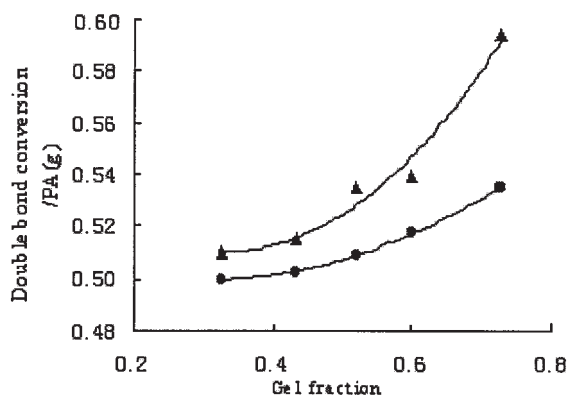
Further, to elucidate the curing mechanism of the divinyl ether and onium salts system, the different inhibitors are added to the curing reaction for finding kinds of initiating active species. Similar to divinyl ether irradiated in the absence of pyridinium salt, there is no solid gel polymer in the reactive system after ammonia of the cationic inhibitor is added. However, the gel yields decrease with concentration of inhibitor increasing in the presence of p-benzoquinone of the free radical inhibitor. When p-benzoquinone is added to 0.2%, the viscosity of the system is close to that of DVE-3. A most viscous substance is only obtained after DVE-3 is irradiated by electron beam in air in the absence of any onium salts and inhibitors. The oxygen in air atmosphere could inhibit the curing reaction of the free radical mechanism. The surface of the gel product is quite dry in the studies in the presence of pyridinium salts in the absence of both free radical and cationic inhibitors. This is an interesting experimental phenomenon. Compared with different experimental phenomena having ammonia, p-benzoquinone, and oxygen, it is discovered that the active centers that induced curing reaction are cations as well as free radicals. The experimental results also show that the whole curing reaction is not influenced by oxygen only when the cationic polymerization possesses some scale in the hybrid polymerization

Therefore, these results demonstrate that the DVE-3 solution incurred radiation-induced cationic polymerization in the presence of pyridinium salts. The conclusion goes along to be the cationic mechanism of polymerization and crosslinking in the curing reaction. The mechanisms in the reaction system might be as follows:

$$DVE - 3 \sim\sim \rightarrow (DVE - 3)^{+\bullet} + e_S^- \qquad (1)$$

$$e_S^- + EIP^+PF_6^- \rightarrow EIP^\bullet + PF_6^- \qquad (2)$$

Figure 5 Relationship of gel fraction and double bond conversion in the gel. (●) Theoretical value; (▲) practical value. 0.3% $EIP^+PF_6^-$ and dry air saturated at 25 °C.
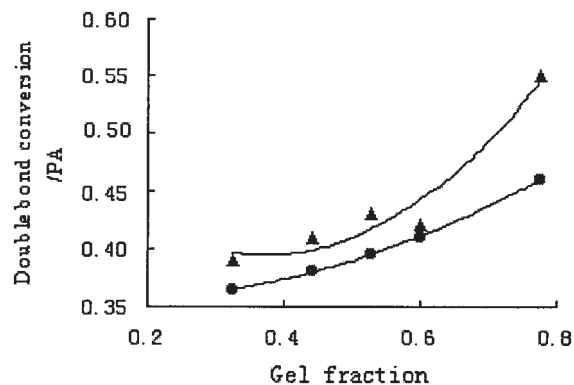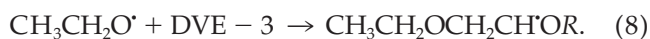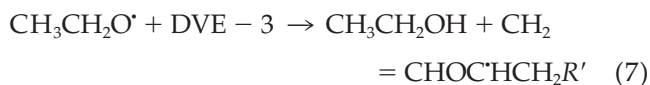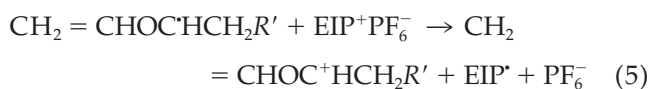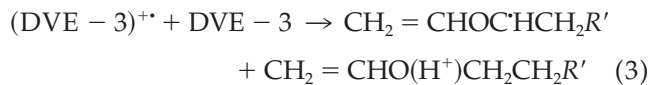
$$(DVE - 3)^{+\bullet} + DVE - 3 \rightarrow CH_2 = CHOC^{\bullet}HCH_2R'$$
$$+ CH_2 = CHO(H^+)CH_2CH_2R' \quad (3)$$

$$(DVE - 3)^{+\bullet} \rightarrow CH_2$$
$$= CHOC^{\bullet}HCH_2OR''CH_2(H^+)OCH = CH_2 \quad (4)$$

$$CH_2 = CHOC^{\bullet}HCH_2R' + EIP^+PF_6^- \rightarrow CH_2$$
$$= CHOC^+HCH_2R' + EIP^{\bullet} + PF_6^- \quad (5)$$

$$EIP^{\bullet} \rightarrow IP + CH_3CH_2O^{\bullet} \quad (6)$$

$$CH_3CH_2O^{\bullet} + DVE - 3 \rightarrow CH_3CH_2OH + CH_2$$
$$= CHOC^{\bullet}HCH_2R' \quad (7)$$

$$CH_3CH_2O^{\bullet} + DVE - 3 \rightarrow CH_3CH_2OCH_2CH^{\bullet}OR. \quad (8)$$

The primary species generated by the divinyl ether compound are still radical cation and electron, owing to the presence of only a small quantity of onium salts in the system. Although the resulting species responsible for the cationic polymerization are carbenium ions but not radical cations, it is believed that radical cations play an important role in radiation-induced cationic polymerization. The radical cations of divinyl ethers are produced by rapid formation processes, subsequently resulting in those of the dimmer radical cations. The dimmer radical cations with hydrogen ion and free radical of carbon distinguishing from common monomers in reaction 3 or 4 initiate cationic polymerization under the proper condition, which are typical radiation-induced cationic polymerization and crosslinking processes. Generally speaking, it is infrequent that activated free cations are generated and induce cationic polymerization without anti-ion in air atmosphere by direct radiation. The ions initiating polymerization will be quenched by impurities in the system so that radiation-induced cationic polymerization usually demands scrupulously dry, oxygen-free, and ultrapure monomers conditions. In the presence of some compounds that can change free radicals into cations with the ability to initiate cationic polymerization and release relative stable nonnucleophilic anions to resist little water and other impurities to inhibit early polymerization, cationic polymerization could take place. Therefore, the oxidation of carbon centered free radicals not only provides an added activated center of initiation but also changes free cationic polymerization into an ion pair initiating reaction. Obviously, the nitrogenous onium salts with low reduction potential not only oxidize α-free radicals by irradiation into cation but also provide relatively stable nonnucleophilic anion PF_6^- for the reaction system enhanced by pyridinium salt. Only if the oxidation potential of the free radicals is lower than the reduction potential of the onium salts is the thermodynamical process feasible. The reduction potential of onium salt $EMP^+PF_6^-$ and $EQ^+PF_6^-$, which are -0.7 and -0.5 V (versus SCE), is greater than the oxidation potential of α-free radicals of isobutyl vinyl ether.[1,14] One important task of the onium salt is the simultaneous release of the counterion (PF_6^-), which stabilizes the carbocation of the vinyl ether against early termination by charge recombination. The nonnucleophilic anion (PF_6^-) can be released in two ways. The first is the fast reaction of solvated electrons, and probably DVE-3 anions with the oniun salt in eq. (2). The second way is reaction of the salt with α-ether radicals in eq. (5), although the counterion (PF_6^-) was not explicitly noted. The reaction is similar to the general mechanism of cationic polymerization, with the exception of initiating course due to the above-mentioned released relatively stable nonnucleophilic anion (PF_6^-). The OCH_2CH_3 radical produced by $EIP^{\bullet}$ radical decomposition in eq. (6) maybe give birth to a new free radical to lead to a kind of chain reaction as the new α-ether radicals may again react with the onium salt in eq. (5) through the hydrogen abstraction reaction in eq. (7) or the additional reaction in eq. (8) in the reactive mechanism. Nevertheless, comparing thermodynamical data of the two equations, eq. (8) is an endothermic reaction, and eq. (7) is an exothermic reaction. The free radical produced by the hydrogen abstraction reaction cannot initiate polymerization because of the conjugative effect of the radical with the π electron of the oxygen atom and double bond. So, eq. (8) seems more feasible. On the other hand, free radicals play an important role in the curing reaction. They not only are oxidized into ion induced cationic polymerization but also themselves possess a certain extent of activity to initiate free radical polymerization. The presence of inhibition of p-benzoquinone and oxygen effect in the system indicates that the oxidation of free radicals competes with direct initiating polymerization at the initial stage. Therefore, the free radicals in divinyl ether might have two different reactions in the system. One is to directly initiate free radical polymerization of multifunctional monomers, and subsequently, the macromolecular free radicals are oxidized into corresponding ions initiating cationic polymerizations. Another is first to be oxidized into carbenium, and the carbenium and the hydrogen ion initiate cationic polymerization. The two polymerizations compete with each other in the system. Only when the quantity of cationic polymerization is greater than that of free radical polymerization does the total reaction exhibit the absence of oxygen effect. All in all, this is a cationic polymerization and crosslinking process, but radicals play an important role in initiation.

CONCLUSIONS

Different from an indirect reactive process of vinyl ether and nitrogenous onium salts in diluted solution, the primary free radicals were directly produced from divinyl ether by electron beam irradiation and the nitrogenous onium salt with the low reduction potential oxidize α-free radicals into corresponding cations initiating polymerizations. Although the primary free radicals might also be produced from collagen in the mixture of collagen and divinyl ether by irradiation, the process doesn't influence oxidization of onium salt to α-free radicals into corresponding cations and subsequent curing reaction. When the curing reaction is initiated by carbenium and hydrogen ion, the gelation point and the gel distribution are similar to the general free radical mechanism of polymerization or crosslinkage. On the basis of the results of the experiments, it seems reasonable to consider that the nitrogenous onium salts only affect the mechanism of initiating the curing reaction and don't influence the gelation point and gel distribution. That is to say, the onium salts change is active center style from free radical into cationic polymerization mechanism. The enhancement comes from the low reduction potential of nitrogenous onium salts. Therefore, this is a pure cationic curing reaction although radicals play an important role in initiation, and the curing reaction shows the absence of oxygen effect.

References

1. Bottcher, A.; Hasebe, K.; Hizal, G.; Yagci, Y.; Stellberg, P.; Schnabel, W. Polymer 1991, 32, 2289.
2. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1980a, 18, 2677.
3. Crivello, J. V.; Lam, J. H. W. J Polym Sci Polym Chem Ed 1980b, 18, 2697.
4. Crivello, J. V.; Lee, J. L. J Polym Sci A Polym Chem 1990, 28, 479.
5. Crivello, J. V. Nucl Instrum Method Phys Res B 1999, 151, 8.
6. Decker, D.; Moussa, K. J Polym Sci A Polym Chem 1990, 28, 3429.
7. Jiang, B.; Yang, L. X.; Zou, Y.; Huang, G. L.; Lin, L. B. Radiat Phys Chem 2002, 63, 469.
8. Lopata, V. J.; Saunders, C. B.; Singh, A.; Janke, C. J.; Wrenn, G. E.; Havens, S. J. Radiat Phys Chem 1999, 56, 405.
9. Malmstrom, E.; Sundell, P.; Hult, A.; Jonsson, S. Nucl Instrum Methods Phys Res B 1995, 105, 168.
10. Pappas, S. P.; Gatechair, L. R.; Jilek, J H. J Polym Sci Polym Chem Ed 1984, 22, 77.
11. Sundell, P.; Jonsson, S.; Hult, A. J Polym Sci A Polym Chem 1991a, 29, 1535.
12. Sundell, P.; Jonsson, S.; Hult, A. J Polym Sci A Polym Chem 1991b, 29, 1525.
13. Sundell, P.; Jonsson, S.; Hult, A. ACS Symp Ser 1990, 417, 459.
14. Schnabel, W. Macromol Rapid Commun 2000, 21, 628.
15. Reichardt, C. Chem Ber 1966, 97, 1769.
16. Wang, M. J.; Dong, L. C.; Du, C.; Ma, R. D. J Radiat Res Radiat Processing (Chinese) 1984, 4, 20.