

New Peracid-Type Polymeric Initiator for Radical Polymerization

GING-HO HSIUE,* TIRNG-LAIR PERNG, and JEN-MING YANG

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 30043, ROC

SYNOPSIS

In this study, a radiation-induced copolymer, namely polyethylene-*g*-acrylic acid powder, was used, whose carboxyl groups can be oxidized to form a highly reactive polymer initiator. The activation energy for its decomposition is 22.4 kcal/mol. It was found that the peracid-type polymeric powder was effective as an initiator for radical polymerization. It had high reactivity toward 2-hydroxyethyl methacrylate (HEMA), which could be easily grafted onto the polymeric powder; also, the homopolymer could be obtained. The kinetic investigation indicated that this polymerization proceeded by a radical mechanism, and the overall activation energy of homopolymerization was 18.67 kcal/mol and the overall activation energy of bigraft polymerization was 17.35 kcal/mol. By using the peracid-type polymeric powder as initiator for the copolymerization of methyl methacrylate with styrene, it was confirmed that the polymerization initiated by the peracid-type polymeric powder was a radical reaction.

INTRODUCTION

A peracid-type polymer was first reported by Helfferich and Luten¹ as an oxygen-transfer resin due to its reactivity with olefins to form diols. They oxidized bifunctional cation exchangers containing carboxylic and sulfonic acid groups with aqueous hydrogen peroxide, which converted the carboxylic acid to percarboxylic acid. Takagi² prepared peracid-type resins without sulfonic acid from the commercial carboxylic acid type resin. The characteristics of the peracid-type resins was further studied by Takagi.^{3,4} One major disadvantage of the above-mentioned peracid-type resins was their instability, i.e., detonation with great violence may occur.

Aside from their function as polymeric reagent for hydroxylation or epoxidation, Koyama et al.⁵ found that the peracid-type resins were effective as an initiator for polymerization of methyl methacrylate. The homopolymers were of concern in their kinetic study.

In our previous studies,⁶⁻⁹ a different type of peracid resin was prepared based on polyethylene-*g*-

acrylic acid in the form of a membrane, particulate, or tube. The carboxyl groups of the grafted acrylic chains were oxidized into peracids.⁶ The stability and the activation energy of decomposition of grafted peracid-type resin were also studied.⁷ Then, 2-hydroxyethyl methacrylate (HEMA), an excellent monomer for a hydrogel, which can be used as biomedical material, was used as second monomer to be grafted on the peracid polymer to form a novel bigraft copolymer. The morphology and properties of the bigraft membrane were investigated,⁸ and their potential applications for biomaterial were discussed.⁹ In this study, the grafted peracid-type resin was synthesized from raw material PE powder. The decomposition stability of this kind of grafted peracid-type powder was further discussed, and their potential applications acting as a radical polymeric initiator of vinyl monomers were also studied.

EXPERIMENTAL

Polyethylene (PE) powder, 40 mesh, was grafted with acrylic acid to form PE-*g*-AA with a content of 100% grafted acrylic acid and subsequently converted to its peracid type. The grafting and peracidification processes were the same as in our previous

* To whom correspondence should be addressed.

publications.⁶⁻⁹ HEMA was dried over alumina and then vacuum-distilled in the presence of Cu_2Cl_2 as an inhibitor. Methyl methacrylate and styrene monomer were washed with 5% aqueous NaOH to eliminate the inhibitor; after washing with water, the monomers were dried over CaH_2 and distilled under reduced pressure. Solvents were purified by ordinary methods, avoiding contamination with moisture.

Determination of Oxidation Capacity

The percarboxylic acid contents of the oxidized powder were determined by reaction with aqueous KI solution and titration of the generated iodine with 0.5*N* sodium thiosulfate.⁸

Polymerization Procedure and Analysis of the Polymers

Peracid-type powder, solvent, and monomer were placed in a 250-mL two-neck bottle and purged with nitrogen. The bottle was kept in a thermostat at a given temperature and stirred with a magnetic stirrer.

In this study, the peracid-type polymeric powder was thermally decomposed into two free radicals,

$$\begin{array}{c} \text{O} \\ || \\ \text{P}-\text{C}-\text{O} \end{array}$$
 i.e., $\text{P}-\text{C}-\text{O}$ (P: polymer) and HO as described in previous work.^{5,6} So the homopolymerization occurred in the solution and the bigraft polymerization occurred at the peracid powder. For a detailed description, the following definitions were used.

Conversion of Monomer to Homopolymer for Homopolymerization, %

$$\% = \frac{\text{weight of homopolymer}}{\text{initial weight of monomer}} \times 100$$

Rate of Homopolymerization, R_h

R_h = the consumption of monomer concentration consumed per second for homopolymerization.

Degree of Grafting for Bigraft Polymerization, % Graft

$$\% \text{ graft} = \frac{W_1 - W_0}{W_0} \times 100,$$

where W_0 is the initial weight of the peracid type polymeric powder and W_1 is the weight of the graft copolymer.

Rate of Bigraft Polymerization, R_g

R_g = the degree of grafting per hour for bigraft polymerization.

Differential Scanning Calarimetry (DSC)

The peracid-type polymeric powder and PE-*g*-AA powder were weighed and put on an aluminum pan. The measured temperature range was 300–460 K. The heating rate was 10°C/min. The peracid content was calculated according to the previous work.⁷

RESULTS AND DISCUSSION

Properties of Peracid-Type Polymeric Powder

The peracid content can be measured by using DSC⁷ because thermal decomposition of carboxylic peracid is exothermic. Its enthalpy is proportional to the peracid content. Figure 1 shows the typical DSC traces of oxidized polymeric powder. Curve 1 shows that an exothermic reaction occurs. Curve 2 is the curve of the PE-*g*-AA powder. Only one endo-

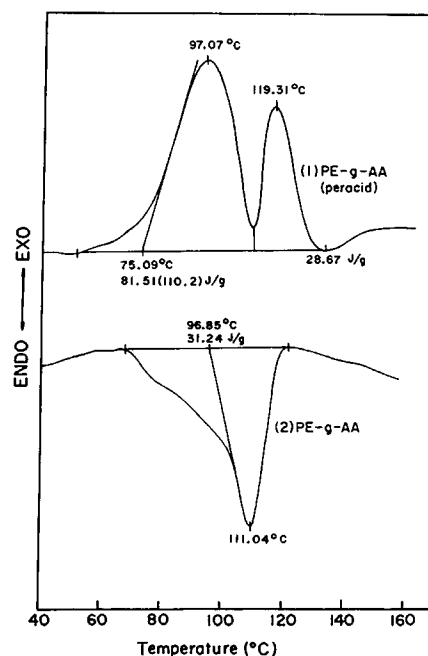


Figure 1 Thermal analysis of the peracid resin by DSC.

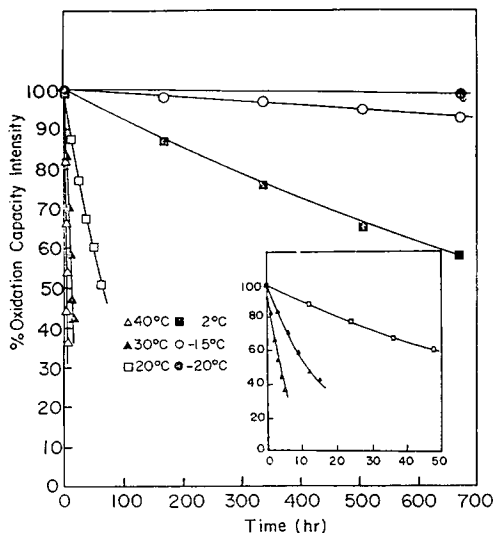


Figure 2 Effect of temperature on storage lifetime of peracid-type PE-g-AA.

thermic curve appears, which is due to the crystalline melting.

Stability of the Peracid-Type Polymeric Powder

From Figure 2 it is apparent that the peracid groups will decompose when stored at temperatures above 20°C and is comparably very stable at -20°C. From the kinetics of decomposition, a first-order rate constant could be obtained. By plotting the rate of decomposition with reciprocal temperature, as shown in Figure 3, the activation energy of decomposition

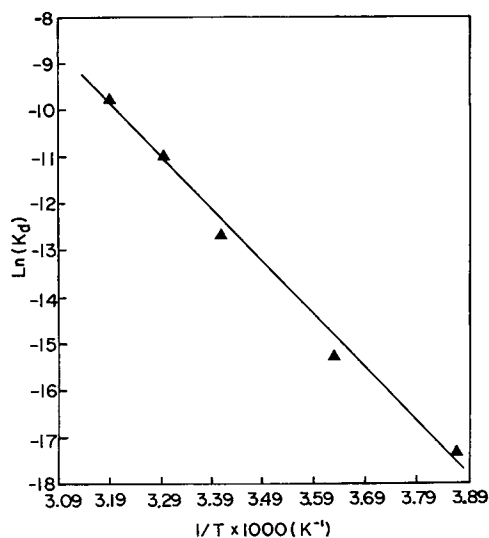


Figure 3 Arrhenius plot for the decomposition of peracid resin.

E_d could then be calculated to be 22.4 kcal/mol. This value is considerably lower than that obtained with peroxide-type initiator, such as benzoyl peroxide.¹⁰

Peracid-Type Polymeric Powder Used as Initiator for the Polymerization of HEMA

Effect of Initiator and Monomer Concentration on the Rate of Polymerization

Figure 4 shows the relationships between the rates of polymerization and the square root of the initiator concentration at constant concentration of HEMA. It is found that both rates of homopolymerization and grafting are proportional to the square root of initiator concentration. The relationships between the rates of polymerization and the concentration of HEMA at constant concentration of the peracid-type initiator are given in Figure 5. Both rates of homopolymerization and grafting are proportional to the concentration of HEMA. These facts indicate that HEMA does not participate in the formation of initiating radical. These results suggest that the polymerization induced by the peracid type initiator proceeds through a radical mechanism.

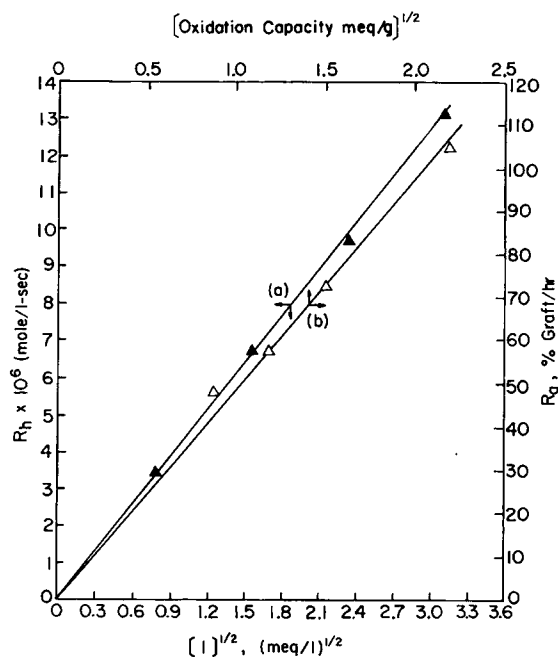


Figure 4 Dependence of the rate of (a) homopolymerization R_h and (b) grafting R_g of HEMA on the square root of initiator concentration $[I]$ at 70°C in ethanol. $[HEMA] = 1.66 \text{ mol/L}$; $[I] = 2.41 \text{ meq/L}$; resin oxidation capacity = 4.81 meq/g.

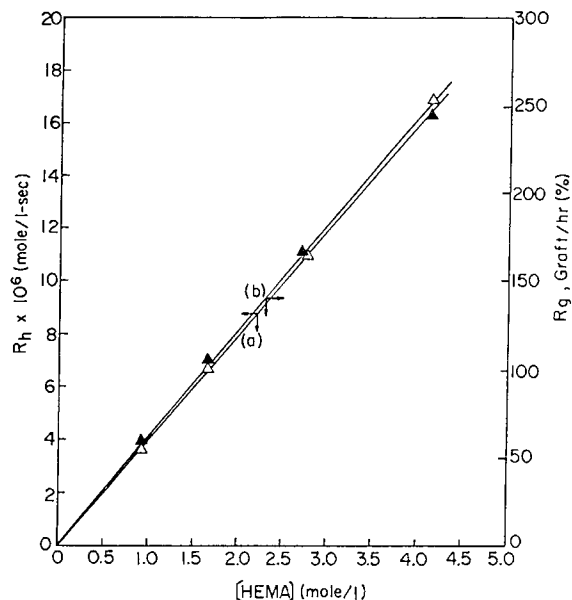


Figure 5 Plot of the rate of (a) homopolymerization R_h and (b) grafting R_g vs. monomer concentration at 70°C in ethanol. $[I] = 2.41$ meq/L; resin oxidation capacity = 4.81 meq/g.

Overall Activation Energy of Polymerization of HEMA

Both homopolymerization and grafting of HEMA initiated by the peracid-type initiator were carried out at various temperatures; the time-conversion curves are given in Figure 6. Then the values of overall activation energy for both homopolymerization and grafting of HEMA with the peracid-type initiator were determined. From the Arrhenius plots as shown in Figure 7, the overall activation energy of homopolymerization was obtained as 18.67 kcal/mol and the overall activation energy of grafting reaction of HEMA was 17.35 kcal/mol. These values are considerably lower than that obtained with peroxide-type initiator, such as benzoyl peroxide.

Effect of Solvent

The effect of solvent on the grafting of HEMA is shown in Figure 8. The graft degree is highest for 1,4-dioxane solvent system and lowest for ethanol system. It was found that the solution of 1,4-dioxane solvent system turned to turbid after the graft polymerization but the solutions of ethanol and *t*-butanol alcohol were still clear. That could be explained by the Trommsdorff effect. The difference of solubility parameter between 1,4-dioxane and polyacrylic acid, which was the base polymer in the peracid-type initiator, is highest in Table I. 1,4-Dioxane is a medium

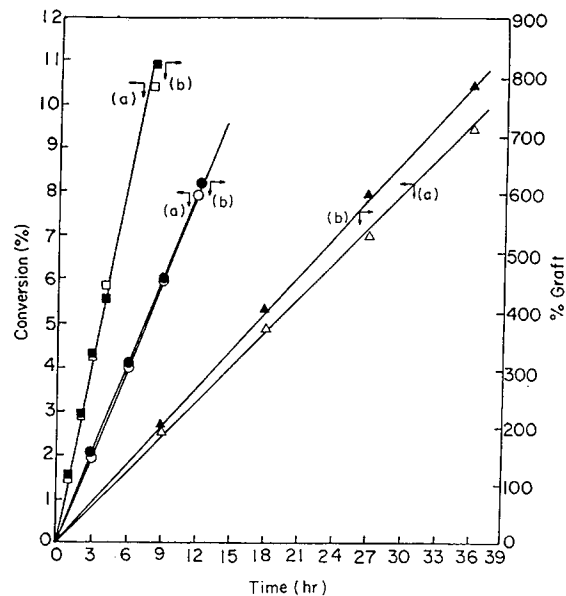


Figure 6 Plots of (a) conversion of homopolymerization and (b) degree of grafting of HEMA at various temperatures in ethanol. $[HEMA] = 1.66$ mol/L; $[I] = 2.41$ meq/L; resin oxidation capacity = 4.81 meq/g.

hydrogen bonding solvent, whereas ethanol *t*-butanol and polyacrylic acid have strong hydrogen bonding. Hence, the compatibility between solvent and peracid-type initiator is least for 1,4-dioxane system, which reduced the chain mobility of polymer, and the termination rate is lowest for the 1,4-

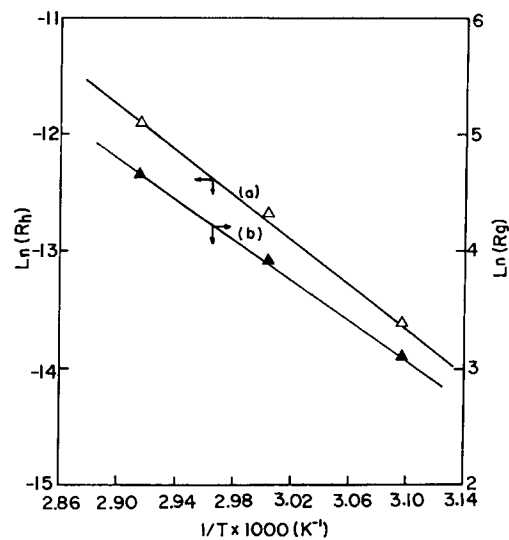


Figure 7 Arrhenius plot for the rate of (a) homopolymerization R_h and (b) grafting in ethanol. $[HEMA] = 1.66$ mol/L; $[I] = 2.41$ meq/L; resin oxidation capacity = 4.81 meq/g.

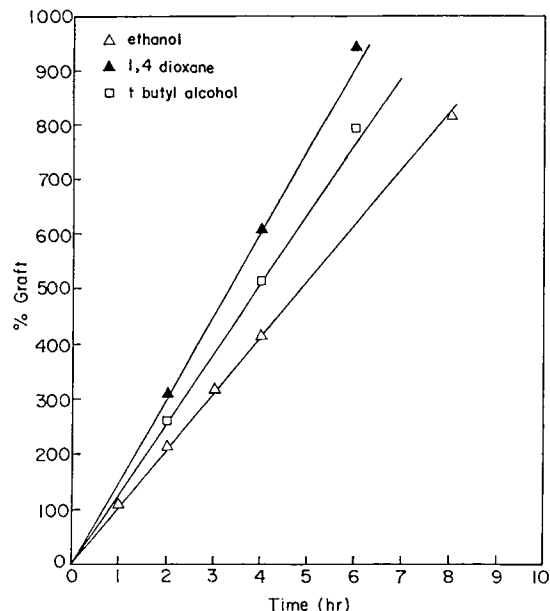


Figure 8 Plots of degree of grafting HEMA for various solvent at 70°C. [HEMA] = 1.66 mol/L; [I] = 2.41 meq/L; resin oxidation capacity = 4.81 meq/g.

dioxane system. Therefore, the graft degree in highest for 1,4-dioxane system.

Determination of \bar{M}_n and \bar{M}_w

The intrinsic viscosities of the homopolymers of HEMA were determined by viscosity measurement on their dilute DMSO solutions at 30°C in an Ubbelohde viscometer. From Figure 9, $[\eta]$ is equal to 0.89 dL/g. By using Mark-Houwink equation $[\eta] = K_m \bar{M}^a$ and

$$K_m = 2.76 \times 10^{-5}, \quad a = 0.84 \text{ for } \bar{M}_n^{11}$$

$$K_m = 12.9 \times 10^{-5}, \quad a = 0.69 \text{ for } \bar{M}_w^{11}$$

Table I Solubility Parameters of Polymers and Solvents

Solvents and Polymers	Solubility Parameter δ (J/m ³) ^{1/2}
Ethanol	26.1 (s)
t-Butyl alcohol	22.7 (s)
1,4-Dioxane	20.7 (m)
Poly(acrylic acid)	24.8 (s) ^a
PE-g-AA (100% grafted)	20.3 (s) ^a

^a Calculated from group contribution theory.
s, strong hydrogen bonding; m, middle hydrogen bonding.

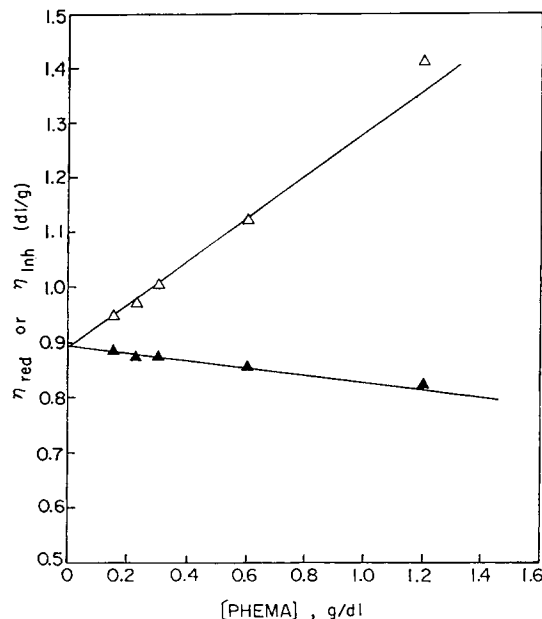


Figure 9 The determination of intrinsic viscosity of PHEMA in DMSO solution at 30°C.

the \bar{M}_n is equal to 23×10^4 and \bar{M}_w is equal to 36×10^4 . These are similar to the molecular weight of polyHEMA initiated by radical polymerization.

Peracid-Type Polymeric Powder used as Initiator for the Copolymerization of Methyl Methacrylate with Styrene

To confirm that the polymerization initiated by the peracid-type initiator is a radical reaction, copolymerization of methyl methacrylate and styrene was carried out. Monomer reactivity ratios calculated by the Fineman-Ross method are given in Table II. It is found that the reactivity ratios are the same as those induced by AIBN initiator. So it is confirmed that the copolymerization of MMA with styrene induced by peracid-type initiator proceeds through a radical mechanism.

From the above discussion, both homopolymerization of HEMA and grafting of HEMA onto peracid-type PE-g-AA and copolymerization of MMA with styrene could be induced by the peracid-type initiator proceeded by a radical mechanism. This indicates that hydroxyl radicals are formed in the decomposition of the peracid group. The mechanism of initiation with peracid-type initiator might be considered as follows:

Decomposition

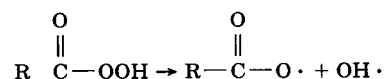
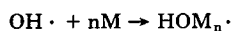
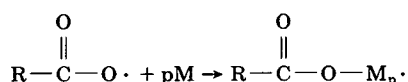


Table II Reactivity Ratio of Styrene (M_1) and MMA (M_2)

Initiator	Temperature, °C	r_1	r_2	Ref.
AIBN	60	0.52	0.46	12
SnCl ₄	20	10.50	0.10	13
PhMgBr	-30	0.05	14.00	14
Peracid-type resin	60	0.67	0.52	5
Peracid-type PE-g-AA	60	0.54	0.46	this work

Propagation for Homopolymerization**Propagation for Graft Polymerization**

The relative ratios of graft polymerization to homopolymerization are listed in Table III. It shows that the grafting efficiency is higher for HEMA than that for MMA and styrene. That may be due to the affinity of HEMA to the polar peracid initiator, which had more compatibility with HEMA than with styrene and MMA. Table III also shows that the rate of homopolymerization is higher than that of graft polymerization. That means the reactivity of RC=O radical for initiation of graft polymerization is much less than that of the hydroxyl radical in the liquid layer, indicating that polymerization is initiated predominantly by the hydroxyl radical in the liquid layer.

Table III Ratio of Grafting Rate to the Rate of Homopolymerization

Monomer	R_{gh}
HEMA	0.17 (in ethanol)
MMA	0.06 (in 1,4-dioxane)
Styrene	0.01 (in 1,4-dioxane)

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