

# Radiation-Induced Polymerization of Butyl Acrylate for Recovery of Organic Solvents

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**ABSTRACT:** Radiation-induced polymerization of butyl acrylate using  $^{60}\text{Co}$  gamma rays has been investigated under different conditions, such as irradiation dose (0–130 kGy), dose rate (10 kGy/h), and temperature (25–70°C). A linear relationship between conversion and temperature of irradiation was found. The activation energy ( $E$ ) of 9.37 kJ/mol was obtained from kinetic analysis of the result from the polymerization at 10 kGy/h. Thermal properties were examined using differential scanning calorimetry and thermal gravimetric analysis. Efficient extraction of organic

solvents including chloroform, chlorobenzene, carbon tetrachloride, benzene, styrene was revealed by the swelling and releasing measurements. These results indicate the feasibility of applying this polymer, which was prepared by radiation-induced polymerization, to management of organic wastes in the field of environment. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3623–3627, 2010

**Key words:** butyl acrylate; gamma radiation; polymerization; activation energy; swelling; releasing

## INTRODUCTION

Gamma radiation has been applied extensively for initiating polymerization reaction, grafting polymer chains onto polymeric backbones, modifying polymer blends and preparing interpenetrating polymer networks.<sup>1–4</sup> Radiation-induced polymerization, as a branch of science, had its beginning in the 1950s.<sup>5</sup> It can result in the formation of three-dimensional polymer networks or branched polymers depending on the structure of the exposed monomers. The advantages of initiation by means of the radiation-chemical method is the possibility of polymerizing monomers, which are difficult to be polymerized by conventional methods, the other advantage is the ease and efficiency of carrying out polymerization in the solid state and the polymerization of channel and layer inclusion compounds. Another advantage is the high penetration of gamma radiation, which ensures regular and homogenous initiation throughout the bulk of the solid monomer. It makes possible to prepare polymers of exceptionally high purity that contains no residues of initiators or other additives. The high purity of these polymers may be important for various special applications, in particular, for producing medical implants and tissues for plastic surgery.<sup>6,7</sup>

Poly(Butyl Acrylate) (PBAC) is prepared in general by emulsion polymerization of butyl acrylate (BAC).<sup>8–10</sup> Also the kinetics and mechanism of the first steps of radiation initiated polymerization was studied.<sup>11</sup> In this work, the radiation-induced polymerization of BAC in bulk has been studied. In addition, the thermal properties of this polymer have been examined.

## EXPERIMENTAL

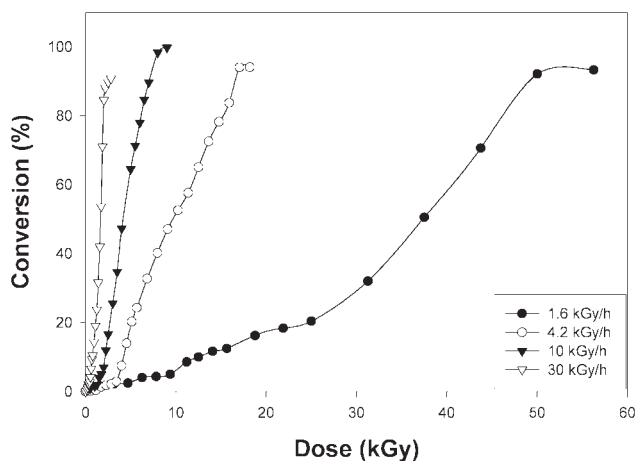
### Polymerization

BAC (Fluka, purity >99%) was used as received. Irradiation was performed in sealed ampoules containing 2 mL of BAC monomers for each, using ROBO facility of  $^{60}\text{Co}$  gamma ray sources arranged in rectangle holder with total activity of (155 kCi) at room temperature in water bath unless stated otherwise to avoid the effect of temperature. Irradiation was carried out at dose rates of 1.6, 4.2, 10, and 30 kGy/h, respectively. All positions used for irradiation were calibrated using Fricke dosimeter. After irradiation, samples were dried in a vacuum oven at 60°C to a constant weight, then weighted. Conversion was then calculated using the following equation:

$$\text{Conversion (\%)} = \frac{W}{W_0} \times 100 \quad (1)$$

where  $W_0$ ,  $W$  are weight of monomer before irradiation and weight of resulting polymer, respectively.

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**Figure 1** Effect of irradiation time on polymerization conversion of butyl acrylate at doses rate 1.6 kGy/h, 4.2, 10, and 30 kGy/h.

### Swelling

The clean and dried PBAC samples of known weights were immersed in different solvents for 48 h. The samples were withdrawn, and immediately weighed upon removed of the solvent on the surface. The swelling percent was calculated as follows:

$$\text{Swelling} = \frac{W_s - W_0}{W_0} \times 100 \quad (2)$$

where  $W_0$  and  $W_s$  represent the weight for dry and swelled samples, respectively.

### Thermal analysis

Thermal analysis of the polymer obtained was performed with the help of Setaram DSC131 apparatus. Calorimetric measurements were made using a nitrogen purge gas under a flow rate of 100 mL/min. at heating rate of  $10^\circ\text{C min}^{-1}$  using about 5 mg of the obtained polymer. Thermal gravimetric analysis was calibrated using nickel, misatherm, and Trafofirm for temperature calibration. Determination of polymerized yield of gel parts was carried out using a Mettler TGA50 apparatus at heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen atmosphere with a flow rate of 100 mL/min.

## RESULTS AND DISCUSSION

### Polymerization of butyl acrylate

The radiation-induced polymerization of BAc in bulk was investigated at dose rates of 1.6, 4.2, 10, and 30 kGy/h at ambient temperature. The conversion obtained under these conditions is shown in Figure 1. The characteristic feature of all curves is a

slow initial rate of conversion, followed by a steep rise and a significant drop in the polymerization after this auto acceleration was observed. The rate of polymerization increased with the increase of the dose rate, due to the increase of free radical concentration with dose rate, which leads to the increase of the initiation rate<sup>5</sup> as given in the following equation:

$$v_i = k_i D^\bullet \quad (3)$$

where  $k_i$  is the rate constant for the elementary initiation reaction.

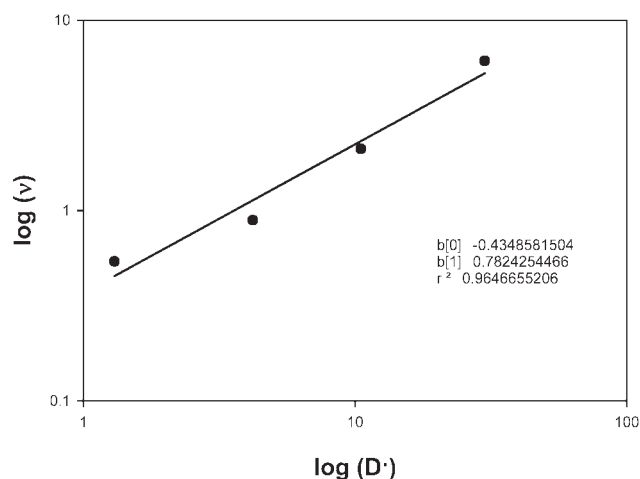
The effect of the dose rate on the polymerization rate is expressed in general by the following equation:

$$v_i = k_i D^{\bullet n} \quad (4)$$

where  $n$  is a constant usually varying from 0.5 to 1. When  $n$  equals 1, this means monomolecular chain is terminated and may indicate that the processes occur by ionic mechanism. The  $n$  values can be determined from Figure 2, which represents the  $\log(v)$  versus  $\log(D^\bullet)$ , and the value is found to be 0.78. This means that BAc is polymerized by the free radical mechanism and the anomalously high value of  $n$  is due to the gel fraction effect.<sup>5</sup>

For measuring the activation energy, the radiation polymerization reaction of BAc was carried out at various temperatures (25, 35, 41, 56, 55, 64,  $70^\circ\text{C}$ ) at dose rate of 10 kGy/h and dose of 10kGy. Arrhenius equation (5) has been used to calculate the activation energy by plotting the logarithm of rate of polymerization vs.  $(1000/T)$ , as shown in Figure 3. Therefore the activation energy can be calculated from the slop multiplied by  $R$ .

$$v = A e^{-E_a/RT} \quad (5)$$



**Figure 2** Plot of  $\log(v)$  vs.  $\log(D)$ .

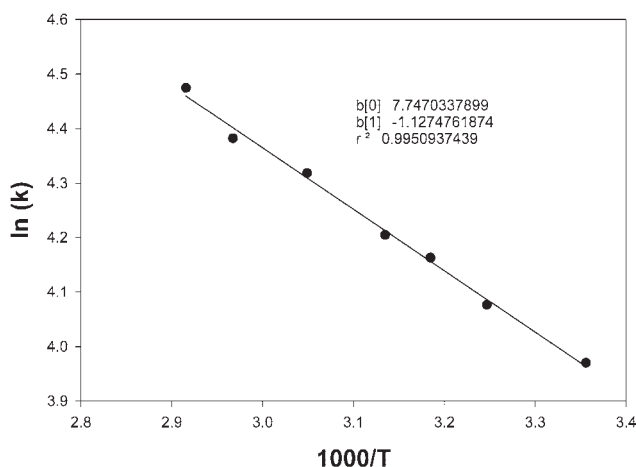


Figure 3 Plot of  $\ln(k)$  vs.  $1000/T$ .

where  $v$  is the rate of polymerization,  $A$  is the pre-exponential factor,  $E_a$  activation energy,  $T$  irradiation temperature in Kelvin.

The activation energy was found to be 9.37 kJ/mol.

### Thermal analysis

Thermal behavior of PBAC was studied using Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA) techniques to detect glass transition temperature ( $T_g$ ) and thermal decomposition temperature of PBAC (Figs. 4 and 5). One can notice that for the sample studied, there is one thermal phenomenon called the glass transition. As for the other wholly amorphous polymers, this transition is the sole observable thermal phenomenon in the scanned temperature, which was found to be at  $-55^\circ\text{C}$ . The results of TGA analysis show that there is one step mass loss at  $300^\circ\text{C}$  due to the random main scission

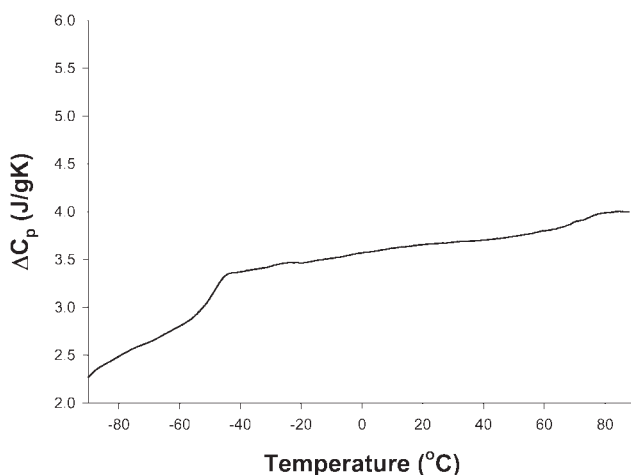


Figure 4 DSC diagrams of poly(butyl acrylate) obtained.

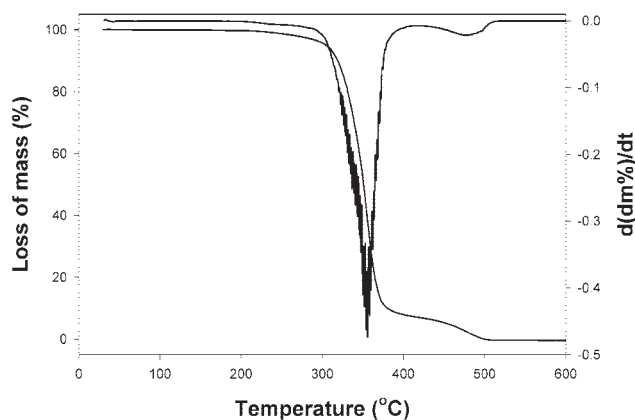


Figure 5 TG and DTG diagrams poly(butyl acrylate) obtained.

of C—C bonds<sup>12</sup> leading to the formation of a carbonaceous residue of about 7% above  $400^\circ\text{C}$ .

### Swelling measurement

The PBAC is well known as a hydrophobic polymer, but it may swell with organic solvents, such as chloroform and benzene. First, the swelling of PBAC in organic solvents, such as phenol dissolved in water was investigated. The clean and dried PBAC sample of known weight was immersed in an ampoule of 25 mL of solution of 5% phenol dissolved in water for 48 h. The results obtained are shown in Figure 6. The swelling in aqueous solution of phenol increases with the time upto 24 h, and then tend to level off above 24 h. It reaches the maximum value of 137% after 48 h.

Swelling of PBAC in different organic solvents, such as chlorobenzene, chloroform,  $\text{CCl}_4$ , benzene, styrene phenol, and  $n$ -hexane was carried out, and the results obtained are shown in Figure 7. It can be seen that the swelling increases with time and

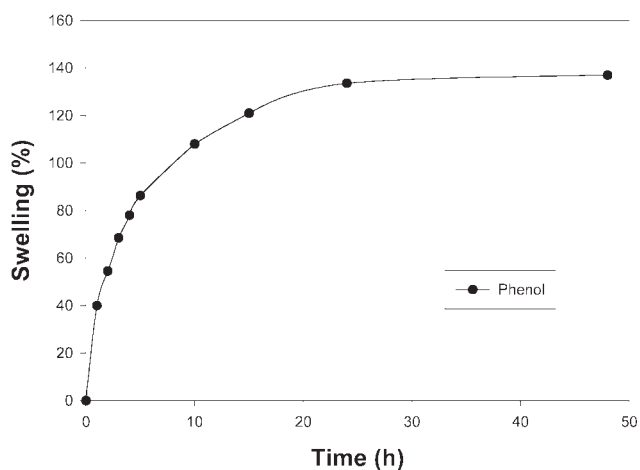


Figure 6 Swelling measurement for the poly(butyl acrylate) obtained for phenol dissolved in water.

attained its equilibrium swelling value after 24 h. Three groups of these solvents could be distinguished; the first is phenol and *n*-hexane and their maximum values are around 100%. The second is benzene and styrene and their maximum values are around 1000%. The last group is CCl<sub>4</sub>, chloroform, and chlorobenzene and their maximum values are around 2000%. These results can be explained according to the relationship between solubility and swelling as shown in the following equation,<sup>13</sup> where surface tension and solubility parameter are related:

$$\delta = 2.1K \left[ \frac{\gamma}{V^3} \right]^a$$

where:

$\delta$ : Hildebrand solubility parameter

$K, a$ : constants

$\gamma$ : surface tension

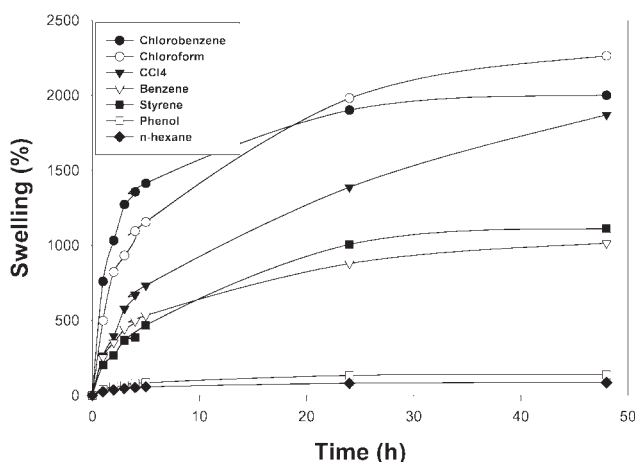
$V$ : molar volume of the solvent

Thus, chlorobenzene ( $33.0 \pm 3.0$  dyn/cm<sup>3</sup>) with the higher surface tension has the highest swelling. Chloroform, in spite of its low surface tension ( $28.9 \pm 3.0$  dyn/cm<sup>3</sup>) has a better swelling property due to low molar volume ( $79.5 \pm 3.0$  cm<sup>3</sup>) compared with carbon tetrachloride with the higher surface tension ( $35.2 \pm 3.0$  dyn/cm<sup>3</sup>) and higher molar volume ( $90.6 \pm 3.0$  cm<sup>3</sup>).

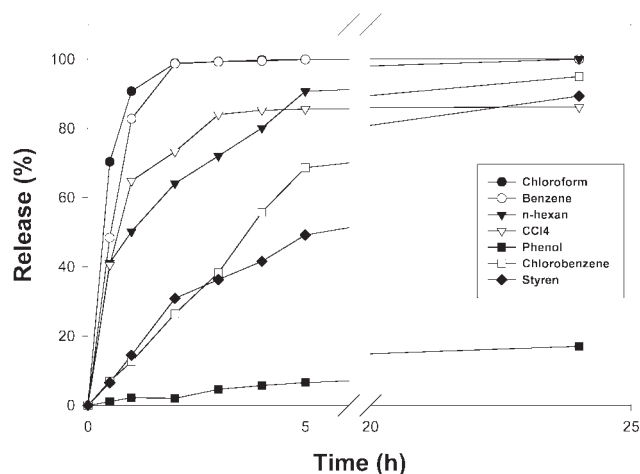
The lowest swelling of *n*-Hexane can be explained by the low surface tension ( $20.3 \pm 3.0$  dyn/cm<sup>3</sup>) and high molar volume ( $172.5 \pm 3.0$  cm<sup>3</sup>).

### Releasing measurements

The releasing of organic solvent in swollen PBAC was investigated in all solvents studied. Such release was carried out and the results obtained are shown



**Figure 7** Swelling measurement for the poly(butyl acrylate) obtained for different organic materials.



**Figure 8** Releasing measurement for the poly(butyl acrylate) obtained for different organic materials.

in Figure 8. It could be observed that all organic solvents studied, except the phenol, are released approximately completely after 24 h. The release of chloroform and benzene is faster than the other solvents and are released completely after only 3 h. These results may suggest an important role of PBAC in recovery of the waste organic materials from the waste water and other pharmaceutical applications, such as the releasing of drugs.

### CONCLUSION

BAC was polymerized using gamma radiation with conversion of 99% at 90 kGy. It was observed that the rate of polymerization increases with the increase of the dose rate, and the activation energy was found to be 9.37 kJ/mol. The polymer has a glass transition temperature at  $-55^{\circ}\text{C}$  according to DSC measurement. Decomposition temperature of the obtained polymer was found to be  $300^{\circ}\text{C}$  according to  $T_G$  measurement. As PBAC can recover organic materials and release them completely approximately after 24 h, therefore this polymer can be used for the environmental applications, such as extraction of organic compounds.

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