

Kinetics of Glycolysis of Poly(ethylene terephthalate) Waste Powder at Moderate Pressure and Temperature

S. Mishra, A. S. Goje

Department of Chemical Technology, North Maharashtra University, P.O. Box 80, Jalgaon 425 001, Maharashtra, India

Received 12 November 2001; accepted 7 May 2002

ABSTRACT: The reaction of poly(ethylene terephthalate) waste (PETW) powder with ethylene glycol (EG) was carried out in a batch reactor at 2 atm of pressure and a 220°C temperature. The particle size range of 50–512.5 μm and the reaction time of 40–180 min that are required for glycolysis of PETW were optimized. To avoid the carbonization and oxidation of reactants and reaction products and to reduce corrosion, the reaction was undertaken below 250°C using a lower reaction time. To increase the yield of dimethyl terephthalate and EG, an external catalyst was introduced during the reaction. The degree of depolymerization of PETW was proportional to the reaction time. The reaction

rate was found to depend on the concentrations of liquid EG and of ethylene diester groups in the polyester. A kinetic model was used for the reaction was found to be consistent with experimental data. The rate constant was inversely proportional to the reaction time, as well as the particle size, of PETW. The degree of depolymerization of PETW was inversely proportional to the particle size of PETW. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1569–1573, 2003

Key words: poly(ethylene terephthalate); ethylene glycol; glycolysis; ethylene diester; kinetics; catalyst; depolymerization; particle size

INTRODUCTION

The larger application of poly(ethylene terephthalate) (PET) in different areas creates its polymerous waste (PETW). Wide-scale PET recycling like traditional materials such as glass, paper, or metals is very economical and ecological viable. The recycling of PETW can be carried out in many ways. Historical and practical reasons cause the processes of chemical depolymerization of PETW to usually be divided into methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and other processes. The glycolysis process is widely used on a commercial scale. The reaction of PETW with ethylene glycol (EG) is of great importance in the commercial depolymerization of high-molecular weight (MW) PET polymer. The yield and quality of the product are strongly influenced by the kinetics and equilibrium of this reaction. For this reason, early studies focused on the kinetics of the overall depolymerization reaction and on the determination of equilibrium constants.^{1–3} Appreciable amounts of monomers were recovered by this method. Glycolysis of PETW is clearly a heterogeneous reaction at temperatures below its melting point (ranging from 250 to 264°C). Because the reaction at temperatures below the melting point proceeds at the solid–liquid interface, the effect of changing the effective surface area of PETW on the reaction should be significant. Such con-

siderations for a heterogeneous reaction have not been discussed from the researchers' perspective. Challa^{1–3} found that the reverse or glycolysis rate is important in determining the maximum extent of depolymerization (below 240°C). He determined that the glycolysis rate is first order with respect to the EG concentration, in which EG does not have any role as internal catalyst. In recent years, glycolysis has been studied as a mean of obtaining polyols from PETW to be used in the production of unsaturated polyesters and polyethylenes.^{4–7} The current interest in the depolymerization of PETW by glycolysis to recover bis-2-hydroxyethyl terephthalate monomer has led to studies of glycolysis catalysts and the composition of the products from the depolymerization of PET soda bottles.⁸ Chen et al.⁹ have studied the kinetics of the glycolytic depolymerization of PET in a pressurized reactor at temperatures between 190 and 240°C. These authors conclude that the glycolysis rate is second order with respect to the EG concentration and that EG thus acts as both a reactant and catalyst in the glycolysis reaction. These conclusions contradict the earlier findings of Challa.^{1–3} Baliga and Wong⁸ found that zinc compounds have a catalytic effect on glycolysis below 240°C. Lead salts have also been studied as a catalyst for glycolysis of PETW.^{10,11} It has also been reported^{12–16} that EG is a better solvent for PET products and oligomers than water.

To understand the correct kinetics (mainly the reaction order), a study is undertaken in which the glycolysis of PETW powder is examined at 220°C and 2 atm of pressure in the presence of zinc acetate and lead acetate in a batch reactor. The PETW particle size and

Correspondence to: S. Mishra (profsm@redifmail.com).

reaction time are optimized. A kinetic model¹⁶ is used to determine the catalytic effect on the glycolytic depolymerization of PETW. The apparent rate constant is inversely proportional to the reaction time and the particle size of PETW.

EXPERIMENTAL

Materials

The PETW used in the experiment was procured from Garaware Polyesters (Aurangabad, M.S., India). The other materials were neutral water, methanol, EG, zinc acetate, lead acetate and obtained from S. D. Fine Chemicals (India). These chemicals were used as received.

Glycolysis of PETW

All glycolysis reactions were carried out in a closed batch reactor at 220°C and 2 atm. The reaction was carried out by taking 10 g of PETW in 40 mL of EG using 0.002 mol of glycolysis catalyst (i.e., 0.001 mol each of lead acetate and zinc acetate) with four pieces of porcelain for different periods of time ranging from 40 to 180 min. Different particle sizes (50–512.5 μm) of PETW were used for this reaction. The reaction mixture was filtered out and the filtrate was distilled for removal of unreacted EG. The bottom product was methanolized with the addition of 0.002 mol of catalyst (i.e., 0.001 mol each of lead acetate and zinc acetate) for 30 min at 84°C and 2 atm. The product, dimethyl terephthalate (DMT), was cooled, crystallized, and separated from the rest of the materials by the recrystallization technique. Then the DMT was dried at 80°C in an oven and weighed. The EG was separated from the remaining liquid phase by the salting-out method. Both the monomeric products (DMT and EG) were analyzed qualitatively and quantitatively. The percentage of depolymerization of PETW, the yield of DMT, and the yield of EG were determined by gravimetry and defined in the following ways:

depolymerization of PETW (%)

$$= \{(W_{\text{PETW},i} - W_{\text{PETW},R}) / W_{\text{PETW},i}\} \times 100 \quad (1)$$

$$\text{yield of DMT (\%)} = \{m_{\text{DMT},0} / m_{\text{PETW},i}\} \times 100 \quad (2)$$

$$\text{yield of EG (\%)} = (m_{\text{EG},0} / m_{\text{PETW},i}) \times 100 \quad (3)$$

where $W_{\text{PETW},i}$ is the initial weight of PETW, $W_{\text{PETW},R}$ is the weight of unreacted PETW, $m_{\text{DMT},0}$ is the number of moles of DMT, $m_{\text{EG},0}$ is the number of moles of EG, and $m_{\text{PETW},i}$ is the initial number of moles of PETW monomers.

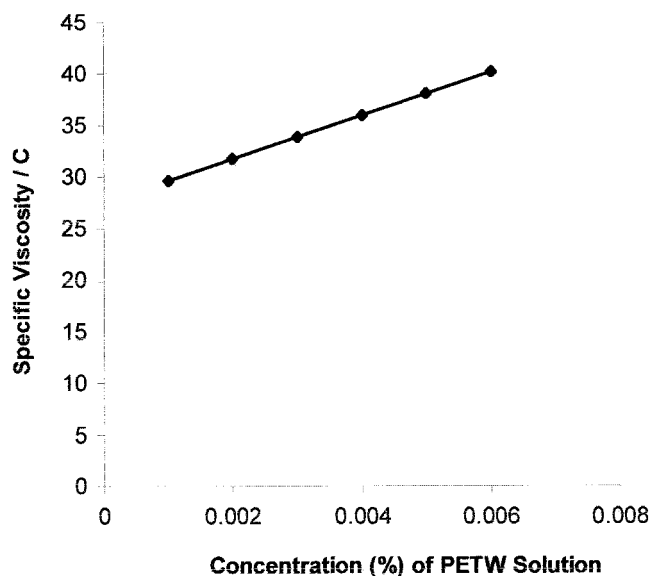


Figure 1 The effect of the concentration of the PETW solution on the viscosity.

Determination of MW

The viscosity-average MW of PETW was determined by the viscosity method. The solvent used was a mixture of phenol and tetrachloroethane in proportions of 3 : 5 (v/v). The effect of the concentration of PETW on the viscosity is shown in Figure 1. The y intercept of this plot was 27.7. Keeping the values¹⁵ of $k = 22.9 \times 10^{-3}$, $\alpha = 0.73$, and y intercept = 27.7 for the mixture, the MW was determined by the relation $[\eta_{\text{sp}}]/C = kM^\alpha$. The MW of the PETW was 16,703.

RESULTS AND DISCUSSION

Optimization of particle size of PETW by glycolysis

The results of the optimization of particle size of PETW for glycolysis methods of depolymerization are shown in Figure 2. Particle sizes ranging from 50 to 512.5 μm were utilized, and we observed that increasing the particle size causes the degree of depolymerization to decrease. Initially the degree of depolymerization is constant and maximum (0.91) for the 50, 64, 90, and 127.5 μm particles but later the degree of depolymerization decreases with increasing particle size; then 0.78, 0.56, 0.32, and 0.22 degrees of depolymerization for particle sizes of 181, 256, 362.5, and 512.5 μm , respectively, are obtained (Fig. 2).

Optimization of reaction time for depolymerization of PETW by glycolysis

When maintaining the particle size of PETW (127.5 μm), the reaction time was optimized by varying the time from 40 to 180 min for the depolymerization reaction of PETW by the glycolysis method. The re-

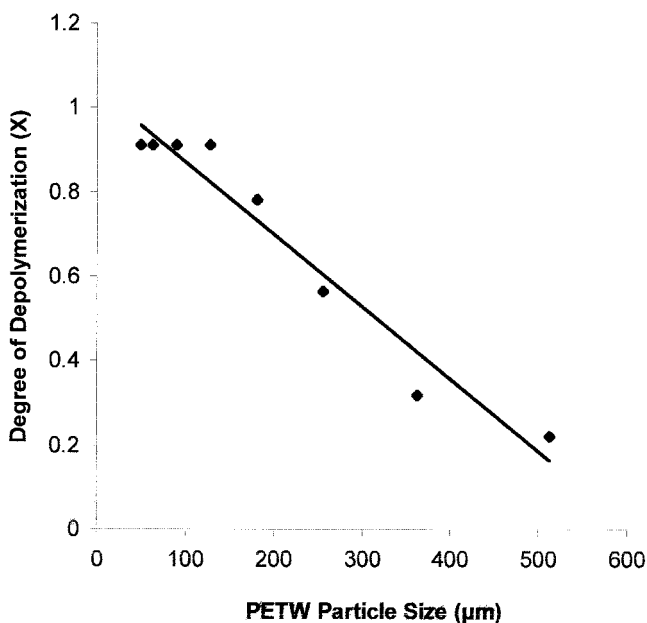
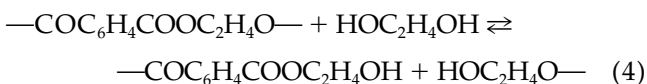


Figure 2 The effect of the PETW particle size on the degree of depolymerization (X).

sults are shown in Figure 3. Initially the degree of depolymerization was less, and increasing the time caused the degree of depolymerization to increase up to a reaction time period of 130 min. After a 140-min reaction time there was no increase in the degree of depolymerization of the polyester waste into the monomeric product. The optimal degree of depolymerization (0.91) was recorded at a 130-min reaction time for the depolymerization of PETW into the optimal monomeric product (Fig. 3).

Kinetic analysis of glycolysis process

Eqs. (1)–(10) are used for kinetic analysis. The glycolysis of PETW takes place at equilibrium and reverse reactions, being the well-known polycondensation, which is given as follows:



In the initial stages of PETW glycolysis, the polycondensation reaction is not important and can be ignored. The rate of glycolysis can thus be expressed as

$$\frac{d[\text{EG}]}{dt} = -\frac{d[\text{EDE}]}{dt} = k_G[\text{EG}]^a[\text{EDE}] \quad (5)$$

where [EG] is the concentration of liquid EG at the reaction temperature, [EDE] is the concentration of ethylene diester (EDE) groups, and k_G is the rate constant for glycolysis. The constant a can have a value of 1 or 2, depending on whether the reaction is internally catalyzed by EG. All concentrations are in moles per liter.

Equation (5) ($a = 1$) was first proposed by Challa¹ (below 240°C). However, the results reported recently by Chen et al.⁹ for the glycolytic polymerization of PET (between 190 to 240°C) suggest that the initial rate of PET glycolysis is proportional to the [EG].² In the very early stages of the reaction, the [EG] and [EDE] in eq. (5) can be approximated by their initial values [EG]_i and [EDE]_i, respectively. Equation (5) can be rewritten to give an expression for the initial depolymerization rate:

$$\text{rate} = k_G[\text{EG}]_i^a[\text{EDE}]_i \quad (6)$$

Chen et al.⁹ used a special form of eq. (6), where [EDE]_i may be considered constant. Therefore, they lumped the [EDE]_i with the reaction rate constant k_G to obtain a new rate constant k_i as shown below.

$$\begin{aligned} \text{rate} &= k_i[\text{EG}]_i^a \\ k_i &= k_G[\text{EDE}]_i \end{aligned} \quad (7)$$

Figure 4 shows the effect of reaction times on the glycolysis rates. In this case the EG concentration is in (mol/mol) PETW repeat units. It is seen that better agreement is obtained with $a = 1$ in eq. (7). The conclusion of Chen et al.⁹ is that the EG catalysis for the glycolysis reaction cannot be justified solely on the data of Figure 4. In a subsequent discussion, eq. (5) will be used to analyze the data obtained in the present work without the assumption of pseudo first-order kinetics used in eq. (7). Equation (5) can be solved by writing a component balance for liquid EG:

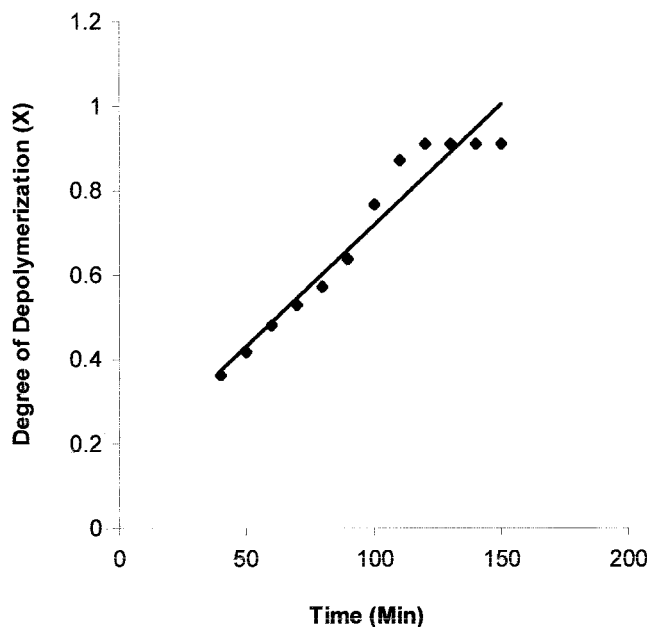


Figure 3 The effect of time on the degree of depolymerization (X).

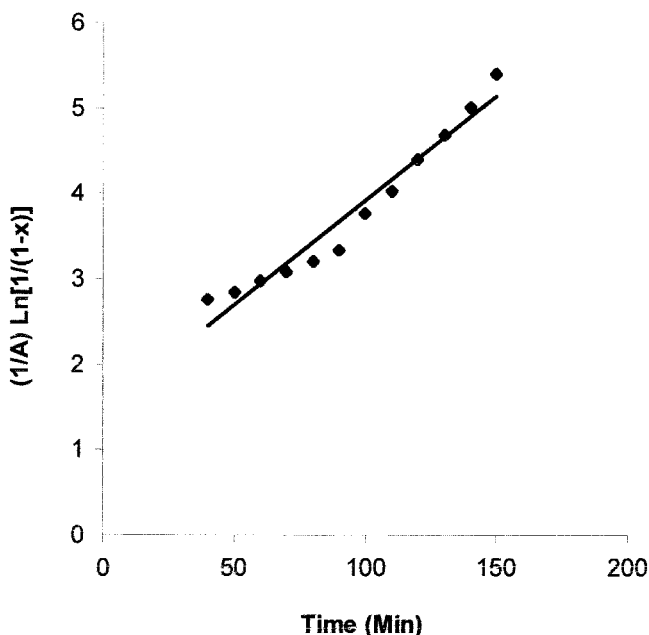


Figure 4 The effect of time on the glycolysis rate.

$$[\text{EG}] = [\text{EG}]_i - [\text{EG}]_{\text{reacted}} \quad (8)$$

According to eq. (4), the amount of EG that has reacted at any time is related by stoichiometry to the amount of EDE groups remaining in the PET:

$$[\text{EG}]_{\text{reacted}} = [\text{EDE}]_i - [\text{EDE}] \quad (9)$$

where $[\text{EDE}]_i$ is the concentration of EDE groups initially present in the polymer. Substituting eqs. (8) and (9) into eq. (5) gives

$$-\frac{d[\text{EDE}]}{dt} = k_G[\text{EDE}](\text{[EDE]} + A) \quad (10)$$

where the constant A is defined as

$$A = [\text{EG}]_i - [\text{EDE}]_i \quad (11)$$

Because the volatility of EG changes with the temperature, the value of A is dependent on the reaction temperature and the reactor vessel volume that is unoccupied by the liquid reactants. Measurements of temperature and pressure in the reactor suggest that a vapor-liquid equilibrium exists in the closed vessel at each temperature. Therefore, the value of $[\text{EG}]_i$ can be readily calculated at each reaction temperature using thermodynamic data for EG¹³ to determine the quantity of EG present as vapor in the 2-L reactor. Figure 5 summarizes the dependency of A on the reaction temperature at 220°C. The variation in this value is about 10%. Equation (10) can be rearranged to separate the variables and integrated between the limits of time

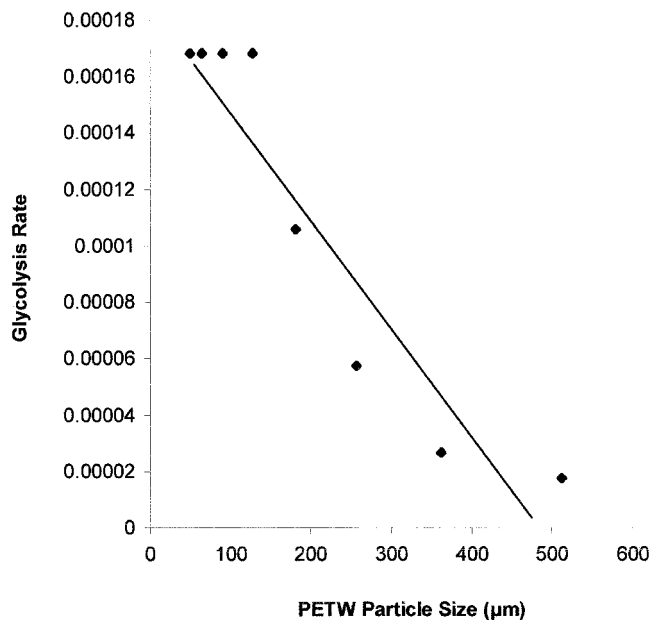


Figure 5 The effect of time on the rate constant (k).

zero and t , and the corresponding EDE concentrations $[\text{EDE}]_0$ and $[\text{EDE}]$, respectively, to give

$$\frac{1}{A} \ln \frac{1}{(1-x)} = k_G t \quad (12)$$

$$x = \frac{A([\text{EDE}]_0 - [\text{EDE}])}{[\text{EDE}]_0([\text{EDE}] + A)} \quad (13)$$

where the variable x represents the degree of conversion or reaction with a value of zero when $[\text{EDE}] = [\text{EDE}]_0$ at reaction time zero and with a value of one when $[\text{EDE}] = 0$. For convenience, reaction time zero is considered to be the time when the reaction tem-

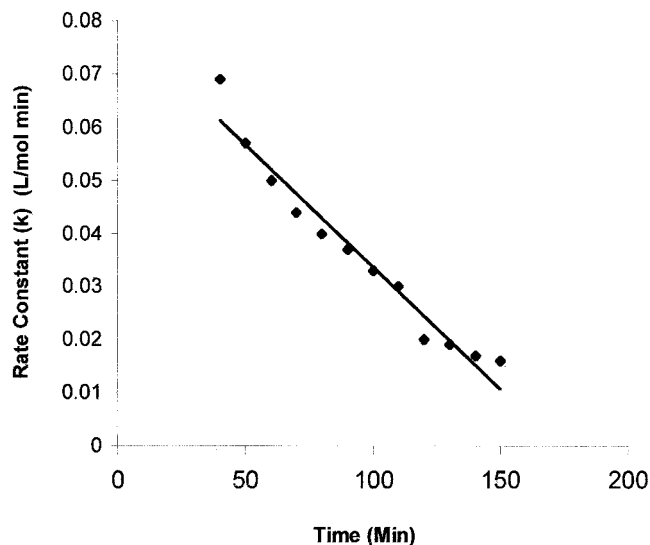


Figure 6 The effect of the PETW particle size on the glycolysis rate.

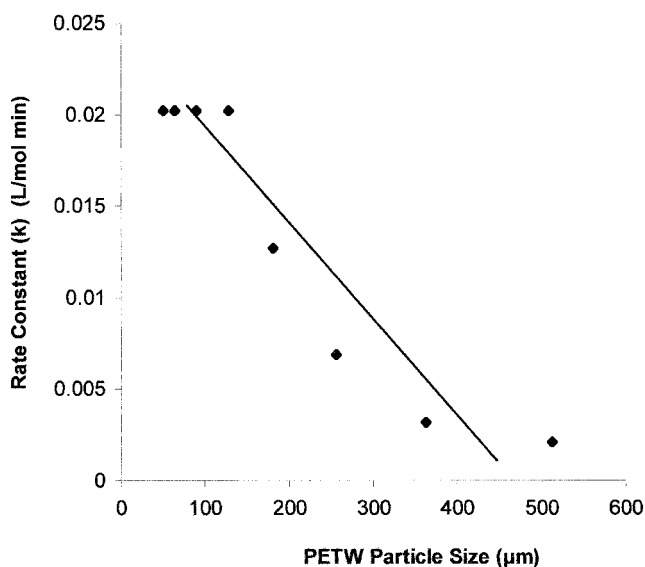


Figure 7 The effect of the PETW particle size on the rate constant (k).

perature is first attained in the reactor vessel. Figure 3 shows a plot of the degree of depolymerization (X) versus the reaction time. The values of $[EDE]$ were calculated from the data using eqs. (8) and (9). The value of $[EDE]_0$ was measured for each set of reaction conditions. This value was employed in eq. (13) to carry out the corresponding kinetic analysis.

The glycolysis rate constant can be obtained by plotting $(1/A)\ln[1/(1-x)]$ versus t , as shown in Figure 4. The initial rate molal equation, eq. (12), provides a good fit for the experimental data. It can thus be concluded from Figures 4 and 6 that the glycolytic depolymerization rate of PETW expressed in eq. (5) is applicable at 220°C. The slope of the line in Figure 4 gives the value of the rate constant. The effect of the reaction time, as well as the PETW particle size, on the glycolysis rate constant are shown in Figures 5 and 7, respectively. It clearly indicates that the glycolysis rate constant is inversely proportional to the reaction time and the PETW particle size.

CONCLUSION

The methods of depolymerization described herein reveal that it is possible to obtain optimal monomeric

recovery with appreciable characteristics from PETW. The optimal reactant size was recorded as 127.5 μm . The degree of depolymerization obtained was 0.91 for the optimal reaction time of 130 min. The yields of DMT and EG were 94.5 and 91.5%, respectively, for the depolymerized PETW. The kinetic model for the glycolytic depolymerization of PETW powder was found close to be first order in both the EG and EDE concentrations. The degree of depolymerization of PETW was proportional to the reaction time. A kinetic model used for the reaction was found to be consistent with experimental data. The results suggest that EG does not have a significant role as an internal catalyst in the glycolytic depolymerization of PETW. Lead and zinc salts appear to have a catalytic effect on glycolysis and seem to influence rates at 220°C. The rate constant was inversely proportional to both the reaction time and the particle size of PETW. The degree of depolymerization of PETW was inversely proportional to the particle size of PETW. The reaction kinetics of the particle size of PETW show that the rate constants and reaction rates decrease with an increasing particle size of the reactant.

References

1. Challa, G. *Makromol Chem* 1960, 38, 105.
2. Challa, G. *Makromol Chem* 1960, 38, 123.
3. Challa, G. *Makromol Chem* 1960, 38, 138.
4. Vaidya, U. R.; Nadkarni, V. M. *J Appl Polym Sci* 1987, 34, 235.
5. Vaidya, U. R.; Nadkarni, V. M. *J Appl Polym Sci* 1988, 35, 775.
6. Vaidya, U. R.; Nadkarni, V. M. *J Appl Polym Sci* 1989, 38, 1179.
7. Johnson, P. L.; Teeters, D. *Polym Prepr* 1991, 32, 40.
8. Baliga, S.; Wong, W. T. *J Polym Sci A* 1989, 27, 2071.
9. Chen, J. Y.; Ou, C. F.; Hu, Y. C.; Lin, C. C. *J Appl Polym Sci* 1991, 42, 1501.
10. Campanelli, J. R.; Cooper, D. G.; Kamal, M. R. *J Appl Polym Sci* 1994, 53, 985.
11. Campanelli, J. R.; Cooper, D. G.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1993, 48, 443.
12. Naujokas, A. A.; Ryan, K. M. U.S. Pat. 5,051,528, 1991.
13. Gallant, R. W. *Physical Properties of Hydrocarbons*; Gulf Publishing; Houston, TX, 1968; Vol. 1, p 109.
14. Chandra, R.; Adab, A. *Rubber and Plastic Waste: Recycling, Reuse and Future Demand*, 1st ed.; C.B.S. Publishers and Distributors: New Delhi, 1994.
15. Gowariker, V. R.; Visavanathan, N. N.; Sreedhar, J. Wiley Eastern Ltd., New Delhi, 3rd reprint, 356, March 1990.
16. Campanelli, J. R.; Karmal, M. R.; Cooper, D. G. *J App Polym Sci* 1994, 54, 1731.