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Kinetics Analysis of the Thermal Decomposition of Poly(Butylene Adipate) Ionomers by Thermogravimetry (TG) and Derivate (DTG) Analysis

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Kinetics analysis and thermal decomposition study of poly(butylene adipate) ionomers (PBAi) synthesized using the dimethyl 5-sulfoisophthalate sodium salt (DMSI) of the diacid monomer were carried out by thermogravimetry (TG) and derivate (DTG) analysis. The decomposition kinetic parameters (activation energy, frequency factor) were calculated. The activation energy values of the PBAi-2, PBAi-3 and PBAi-5 ionomers were respectively found as 164.51, 141.91 and 78.07 kJ/mol. The influence of DMSI content on the decomposition of the ionomers was investigated. The activation energy values decrease with increasing the content of DMSI. This suggests that increasing the content of DMSI makes the thermal decomposition of the ionomers easier.

Keywords thermal analysis, ionomer, kinetic parameters

Introduction

Ionomers have been extensively investigated due to the great interest both from the point of view of basic research in polymer science (1–4) because these are polymeric materials which contain a small percentage of ionic groups attached to a hydrocarbon backbone, and because of their potential application at ambient temperature in ionic devices such as secondary batteries and fuel cells (5–8). Ionomers are usually prepared from basic polymers such as polyesters by introduction of pendant acid groups. Ion conduction is an important advantage of ionomers over other solid electrolytes; they also have unique mechanical and electrical properties and ease of fabrication into films of desirable sizes and interactions to strengthen the electrode-electrolyte contact (9).

Over recent decades, ionomers have been rigorously investigated for their unique characteristics due to the presence of ionic aggregation in organic polymers. Glass transition behavior, morphology, viscoelasticity, and various physical properties of

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polystyrene and polyacrylate ionomers have been intensively studied (10–15). The arrangement of the ion multiplets in a matrix has also been widely explored experimentally and theoretically (16–18). Compared with polystyrene and acrylate based ionomers, far fewer investigations have been undertaken for semicrystalline polymers because the presence of crystallinity, especially at high level, complicates the interpretation of ionic aggregation (19). Ionic interaction between the groups results in significant changes in the physical properties.

In the present work, we investigate kinetic decomposition parameters of ionomers; this information would be helpful to researchers towards applying these materials in different application fields. The study of thermal decomposition, particularly the kinetic parameters have proved to be very useful for elucidation of the thermal properties of these materials. Thermogravimetry analysis (TG) is a technique to study solid decomposition processes including their kinetics. Kinetic studies by the TG method have been extensively reported in the literature (20–23). A number of theoretical models have been proposed to explain the thermal kinetics studies. In calorimetric measurements, two basic methods, isothermal and non-isothermal conditions, can be used. If a material is brought quickly to a temperature above its glass transition, T_g, and the heat evolved during the thermal process is recorded as a function of time, this method is called an isothermal process. Whereas, in a non-isothermal process, the material is heated at a fixed rate and the heat evolved is again recorded as function of temperature and time.

Experimental

The Synthesis of the Ionomers

Apidic acid, 1,4-butanediol, and dimethyl 5-sulfoisophthalate sodium salt (Aldrich) were used without further purification. Titanium tetrabutoxide was purchased from Aldrich and used as received. The poly(butylene adipate) (PBA) and its ionomers were prepared employing a two–step polymerization route. First, calculated amounts of apidic acid and butane diol (1:1.2 by mole ratio) were introduced to a reactor equipped with an overhead stirrer and a temperature control device. The monomer mixture was melted and stirred at 190°C for 2 h evolving water condensate. Then, the reaction temperature was raised to 250°C over a period of 30 min gradually applying reduced pressure to remove low molecular weight condensates and maintained for 7 h at the temperature. Our synthetic route for the PBA ionomer was confirmed by ^{1}H-NMR and the related characterization method. The only way to synthesize ionomers such as PBAi is via a step growth polymerization route. The poly(butylene adipate) samples are denoted by the mole fractions of ionic groups determined from ^{1}H-NMR spectroscopy. For instance, PBAi-3 represents poly(butylene adipate) containing 3 mol% of dimethyl 5-sulfoisophthalate sodium salt (DMSI). DMSI contents in PBA corresponding to the respective feed composition were spectroscopically determined by ^{1}H-NMR study. The results of PBAi synthesis are summarized in Table 1. Physical properties and biodegradation of the poly(butylene adipate) ionomers investigated are described elsewhere (24).

Thermogravimetry (TG) and Derivate Thermogravimetry (DTG)

Thermal behavior of the PBAi ionomers was carried out using a Shimadzu TG-50 thermogravimetry apparatus. The heating rates of 5, 8, 11 and 14°C/min were performed from room temperature to 500°C. A pure nitrogen flow was used with the ionomers.

Table 1
The composition and molecular weight of PBAi series (24)

Ionomer	Molar ratio in feed[a] (adipic acid/DMSI)	Molar ratio in real[b] composition (adipic acid/DMSI)	$M_n \times 10^{-4c}$	$M_W/M_n{}^c$	Ionomer length per molecule
PBAi-2	98/2	98.5/1.5	2.81	2.30	3.26
PBAi-3	97/3	97.0/3.0	2.41	2.16	5.59
PBAi-5	95/5	95.0/5.0	1.59	1.79	6.15

[a] Molar ratio of DMSI to adipic acid in total diacid feed.
[b] Real composition was determined by ^{1}H-NMR.
[c] Determined via gel permeation chromatography (GPC) with polystyrene standards.

Theoretical Background

The kinetic parameters of thermal decomposition of the ionomers can be calculated by the Kissinger method.

The Avrami-Erofeev equation (25) is used to calculate kinetic parameters of the reaction.

$$x = 1 - \exp[-(kt)^n] \tag{1}$$

where x is the fraction of conversion, n is a parameter connected with the mechanism of the reaction, k is the reaction rate constant, which is defined as $k = A\exp(-E/RT)$. In the non-isothermal method, the sample is heated at a fixed rate and the heat evolved is recorded as a function of temperature. The relation between the sample temperature and the heating rate (β) is defined as $T = T_o + \beta t$, where T_o is the initial temperature. The kinetic parameters are obtained by taking the time derivatives of k and Equation 1. The derivatives of k and x are given by:

$$\dot{k} = \frac{dk}{dT}\frac{dT}{dt} = \beta\frac{E}{RT^2}A\exp\left(-\frac{E}{RT}\right) = \left(\frac{\beta E}{RT^2}\right)k \tag{2}$$

$$\dot{x} = n(kt)^{n-1}[k + \dot{k}t](1 - x) \tag{3}$$

$$\dot{x} = n(kt)^{n-1}k\left[1 + \frac{\beta Et}{RT^2}\right](1 - x) \tag{4}$$

Kissinger argued (9, 26) that:

$$\frac{\beta Et}{RT^2} = \frac{E}{RT}\frac{\beta t}{T} \ll 1 \tag{5}$$

which is valid if βt/T$\ll$1. i.e, when the linear change is small compared to the actual temperature. If this happens then we have,

$$\dot{x} = nk^n t^{n-1}(1 - x) \tag{6}$$

Differentiating we obtain (27):

$$\ddot{x} = n^2 k^n t^{n-2}(1-x)\left[\frac{\beta E t}{RT^2} + \frac{n-1}{n} - k^n t^n\right] \tag{7}$$

In this equation, in the case when $n = 1$, which is rather frequent, this allows us to neglect the middle term and then we have,

$$\ddot{x} = n^2 k^{n-1} t^{n-1} k(1-x)\left[\frac{\beta E}{RT^2} - k^{n-1} t^{n-1}\right] = n^2 Bk(1-x)\left[\frac{\beta E}{RT^2} - Bk\right] \tag{8}$$

At the maximum, when $x = 0$,

$$\frac{\beta E}{RT^2} = Bk = BA\exp\left(-\frac{E}{RT}\right) \tag{9}$$

If $T = T_p$ (maximum peak temperature) is taken in Equation 9, this equation can be used to obtain the activation energy using the linear relationship between $Y = ln(\beta/T_p^2)$ and $X = 1/T_p$. The intercept of the straight line can be used to calculate the frequency factor.

Results and Discussion

The dynamic TG curves of the ionomers at different heating rates are shown in Figures (1–3). The thermal stability temperature of the ionomers is defined as the initial decomposition temperature. Ionomers show high thermal stability. Above the initial temperature, the ionomers undergo the thermal decomposition step, which lasts up to the temperature of 500°C. A significant difference in weight loss of the ionomers was not observed when the TG curves were compared with each other. This was attributed to the content of the DMSI and the relative difficulty of decomposition of the PBA containing segments.

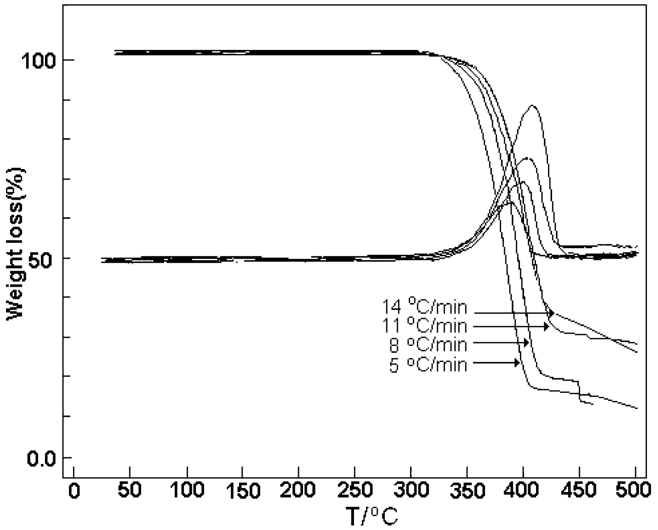

Figure 1. The TG and DTG curves of the PBAi-2 ionomer.

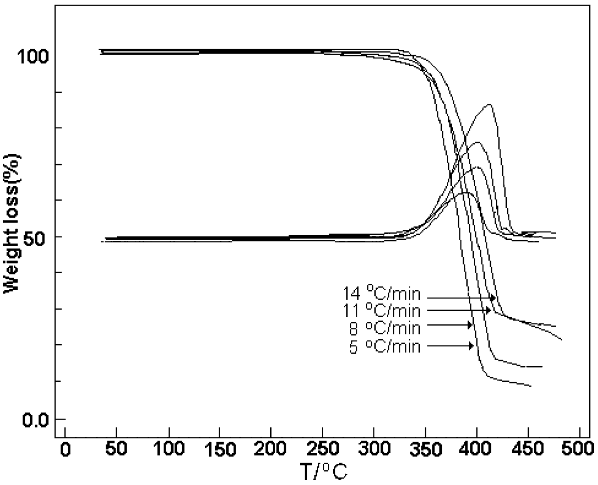

Figure 2. The TG and DTG curves of the PBAi-3 ionomer.

The presence of DMSI does not significantly improve the onset of thermal decomposition temperature. The DTG curves of the ionomers are shown in the same figures. The DTG curves exhibit an exothermic characteristic. The exothermic character of the decomposition is clearly seen causing an increase of the temperature that is significant at high heating rates, i.e, a higher heating rate shifts the weight loss curve to a higher temperature. This suggests that the rate of weight loss at a lower heating rate is lower than that at a higher heating rate because, at a lower heating rate, the time required for ionomers to reach a given temperature was longer than at a higher heating rate (27). In the DTG curves, the value of the DTG peak maximum varies as the heating rate increases. The maximal rate is achieved at the peaks of the DTG curve. The coordinates of this point are T_p and x_p, corresponding to the inflection point of the TG curve. This point can be used to

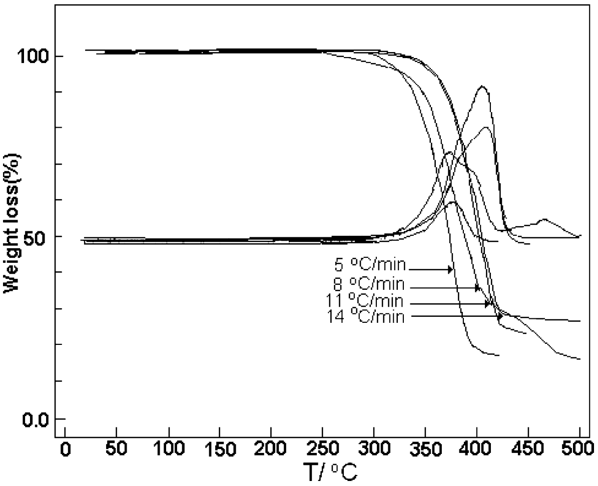

Figure 3. The TG and DTG curves of the PBAi-5 ionomer.

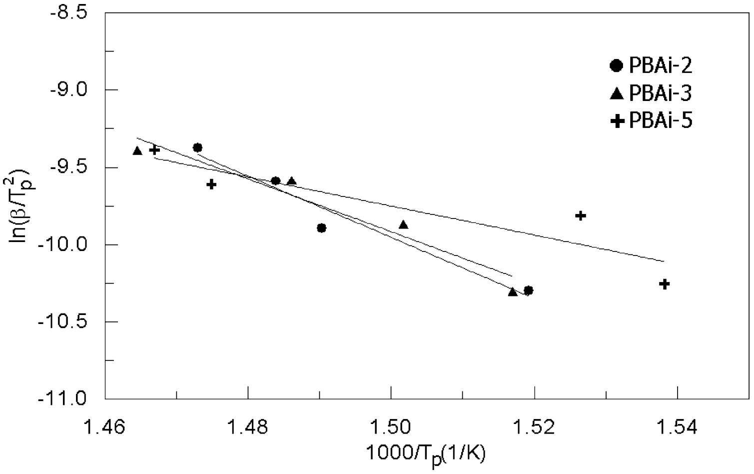

Figure 4. The Kissinger plots of the ionomers.

obtain the activation energy of the ionomers. In order to calculate activation energy, T_p values at various heating rates were determined from the peak position of the DTG curve. The activation energy is calculated from the slope of $ln(\beta/T_p^2)$ vs $1000/T_p$. It is observed that the thermal decomposition does not shift proportionally with increasing heating rates. This can be due to thermal conductivity of the ionomers. It is well known that the thermal conductivity of the polymeric materials is low. Therefore, in the ionomers the temperature gradient occurring when heat is applied does not change linearly with increasing heating rates of 5, 8, 11 and °C/min. That is why, selection of the best model for fitting thermal decomposition kinetics is very important to determine the kinetic parameters of the polymers. We used the Kissinger method to calculate kinetic parameters. This method is one of the most frequently used to obtain kinetic parameters. The activation energies of the thermal decomposition of the ionomers were determined from the plots of $\ln(\beta/T_p{}^2)$ vs. $1000/T_p$, as shown in Figure 4. The activation energy values of the PBAi-2, PBAi-3 and PBAi-5 ionomers were respectively found as

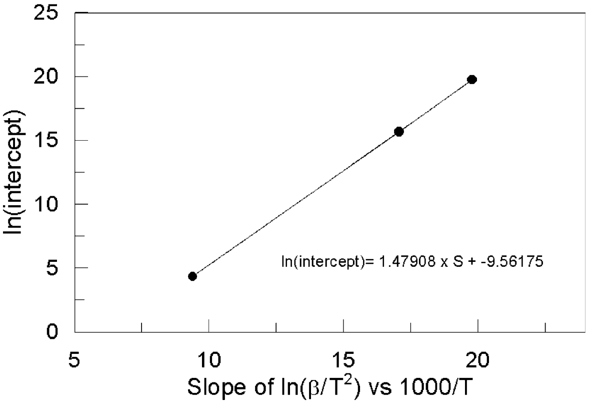

Figure 5. The ln(intercept) vs slope of $\ln(\beta/T_p{}^2)$ vs $1000/T_p$ plot.

164.51, 141.91 and 78.07 kJ/mol. The activation energy values decrease with the increasing content of DMSI. The activation energies calculated show a regular variation with the increasing content of DMSI.

In order to indicate the effect of content of DMSI on the decomposition process, we plotted the intercept (A) values as a function of the slope values (S) (Figure 5) the graph was fit by the following equation,

$$A = C + DS \tag{10}$$

where C and D are constants; The results show that any increase of the activation energy is accompanied by an increase of the frequency factor. It is seen that this relation is valid for the ionomers.

Conclusions

Kinetics analysis and thermal decomposition study of poly(butylenes adipate) ionomers (PBAi) synthesized using the dimethyl 5-sulfoisophthalate sodium salt (DMSI) of the diacid monomer were carried out by thermogravimetry (TG) and derivate (DTG) analysis. The decomposition activation energy values of the PBAi-2, PBAi-3 and PBAi-5 ionomers were respectively found as 164.51, 141.91 and 78.07 kJ/mol. The kinetic parameters (activation energy, frequency factor) were calculated. The kinetic parameters change with the content of DMSI. Consequently, increasing the content of DMSI makes easier the thermal decomposition of the ionomers.

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