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Reaction kinetics of thermoplastic polyurethane polymerization in situ with poly(vinyl chloride)

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Abstract

In this study, the reaction kinetics of thermoplastic polyurethane (TPU) polymerization in situ with poly(vinyl chloride) (PVC) was characterized with differential scanning calorimetry. The presence of PVC appeared to enhance the thermodynamic drive for TPU hard segment phase separation and domain ordering from the PVC/TPU reactant mixture. Prior to hard segment phase separation, and thus some critical conversion, TPU polymerization in situ with PVC obeyed the same nth order, phenomenological kinetic rate law followed by neat TPU polymerization. In addition, the overall rate constant employed in the rate law increased in the presence of PVC. After hard segment phase separation, and the resulting physical cross-linking of the PVC/TPU reactant mixture, the reaction kinetics of TPU polymerization in situ with PVC became diffusion controlled.

Keywords: Reaction kinetics; Thermoplastic polyurethane; Poly(vinyl chloride)

1. Introduction

Blends of poly(vinyl chloride) (PVC) with other polymers, used to produce permanently plasticized or impact modified compounds in the absence of monomeric liquid plasticizers, have significant commercial significance but are often difficult to mix on conventional compounding equipment and command significant premiums. Of these blend systems, PVC/thermoplastic polyurethane (TPU) blends are described in the literature, but are not well known commercially. Remarkable abrasion resistance, permanence, low temperature flexibility, and impact resistance is claimed for such blends which are said to be good candidates for cable jacketing, tubing, hose, and shoe sole applications [1].

Although it is possible to melt blend PVC and softer grades of TPU, the high processing temperatures and melt viscosities required to homogenize such blends often result in partial PVC degradation, even in the presence of thermal stabilizers [2]. While solution blending eliminates many of the problems associated with melt blending, it is not a commercially viable mixing technique due to solvent removal. Consequently, it would be advantageous to develop an alternative blending technique.

In the synthesis of semi-interpenetrating polymer networks [3] and dynamic vulcanizates [4], polymer blending is often achieved by mixing an already polymerized high polymer with miscible monomers or oligomers of a second polymer that are subsequently polymerized. Such a reactive blending technique offers an attractive, alternative method for blending PVC and TPUs. More specifically, blending PVC with TPU monomers with which it is miscible and the subsequent polymerization of high molecular weight TPU in situ with PVC under a set of processing conditions benign to PVC overcomes the previously mentioned melt and solution blending problems. Several other advantages that such a reactive blending technique might offer include reduced costs and a means of controlling final blend morphology.

Few investigations of polyurethanes polymerized in situ with PVC exist in the literature. Parnell et al. [5] developed a novel reactive blending process for producing PVC/TPU blends. Broken down into two fundamental stages, this process included the compounding and plasticization of PVC with the polyol and chain extender of the TPU, and,

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upon adding the TPU diisocyanate, the subsequent polymerization of TPU in situ with PVC to produce a PVC/TPU blend. A result of reaction induced PVC/TPU blend phase separation, the resulting partially miscible blends were characterized by heterogeneous, multi-phase morphologies and exhibited excellent tensile properties intermediate between that of neat PVC and TPU. It was also discovered that the PVC stabilizer catalyzed TPU polymerization.

In order to scale the PVC/TPU reactive blending process described by Parnell et al. [5] up to an industrially viable continuous production process, such as reactive extrusion, a detailed understanding of reaction kinetics is essential. Hence, the objective of this study is to determine what effect neat and stabilized PVC have on the reaction kinetics of TPU polymerization. For comparison, the kinetics of neat TPU polymerization will also be characterized.

2. Experimental

2.1. Materials

The poly(vinyl chloride) (PVC) homopolymer used in this study was obtained from the Oxy Vinyls company, formerly Geon. This injection molding grade, suspension polymerized PVC resin had a number average and weight average molecular weight of approximately 30,000 and 63,000 g/mol, respectively. The PVC stabilizer used in this study, dibutyltin bis(2-ethylhexyl mercaptoacetate) (T31), was obtained from Elf Atochem.

The TPU formulation used in this study was miscible with PVC until high conversions were reached. The soft segment of the TPU was an oligomeric diol of poly(butylene adipate) (PBA) supplied by Bayer. This diol had a number average molecular weight of approximately 2000 g/mol. The hard segment of the TPU was derived from flaked 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) supplied by Bayer and ARCO chemical company, respectively. Synthesized with equimolar quantities of PBA and BDO, the TPU contained 76.84% PBA, 3.536% BDO, and 19.62% MDI by mass (based on PBA with an equivalent number average molecular weight of 979.1 g/mol) when the stoichiometric ratio of hydroxyl to isocyanate functionality was maintained at unity. However, MDI was always used in 2% excess of stoichiometry in an effort to compensate for trace amounts of residual water in the reactants.

In preparation for TPU synthesis, PBA was melted and dried under a vacuum at 100 °C for a minimum of 4 h while BDO was dried over type 3A molecular sieves at room temperature for at least 2 weeks prior to synthesis. MDI was used as received but was stored under a vacuum at 0 °C until required for synthesis. PVC was dried under a vacuum at 60 °C for 12 h to remove trace quantities of water. A domestic, Waring type blender was used to dry blend T31 with PVC.

2.2. Processing equipment and procedures

Kinetic studies of TPU polymerization were conducted on neat TPU and three different PVC/TPU reactant mixture compositions. Regardless of the polymerization environment, the 'one-shot' process was always the preferred route of TPU synthesis. In the synthesis of neat TPU reactant mixtures, dewatered PBA (heated to 100 °C), BDO (at room temperature), and MDI (at room temperature) were gravimetrically metered into a 500 ml polypropylene beaker and vigorously hand mixed for 15 s. For TPU reactant mixtures catalyzed with T31, PBA contained a predetermined concentration of T31. Having thoroughly mixed all TPU reactants, samples were removed and prepared for immediate kinetic analysis.

All three PVC/TPU reactant mixture compositions were prepared on a Brabender batch type internal mixer operated at 50 rpm. Equipped with cam style rotors, this device had an internal mixing volume of approximately 82 cm^3. The internal mixer was always operated with a fill factor of 85% by volume and a mixing temperature of 120 °C. Initially, PVC stabilized with a predetermined concentration of T31 was added to the preheated internal mixer and allowed to equilibrate for 5 min. Next, PBA was added in proportions required to yield PVC/PBA blend compositions of 25/50, 50/50, and 75/25% by weight. After mixing PVC/PBA blends for 9 min, stoichiometric quantities of BDO (depending on composition) were added to yield PVC/PBA/BDO blend compositions of approximately 24/73/3, 49/49/2, and 74/25/1% by weight. Upon producing homogeneous, one-phase PVC/PBA/BDO blends after 15 min of total mixing time, MDI was added and allowed to incorporate for exactly 2 min. In this way, homogeneous, one-phase PVC/TPU reactant mixtures were produced wherein the TPU reactants were substantially unpolymerized. Samples were then removed from the internal mixer and prepared for immediate kinetic analysis.

2.3. Characterization equipment and procedures

A thermal advantage 2920 modulated differential scanning calorimeter operating in the isothermal mode was also used to measure the kinetics of TPU polymerization. In conducting these experiments, samples were carefully weighed to 10 ± 2 mg and sealed in aluminum hermetic pans and lids. Upon placing a sealed sample into the DSC preheated to a specific isothermal temperature, heat flow resulting from the exothermic TPU polymerization reaction was measured as a function of time. After 60 min of isothermal polymerization, samples were immediately quenched to 0 °C at a cooling rate of −100 °C/min and then subjected to a temperature scan from 0 to 200 °C at a heating rate of 20 °C/min. This temperature scan was performed in an effort to quantify any residual heat of reaction not evolved in the previous isothermal scan and to ensure complete TPU polymerization.

3. Results and discussion

3.1. Reaction kinetics of neat TPU polymerization

Most studies investigating the reaction kinetics of urethane formation have adopted the following Arrhenius type, phenomenological rate law

$$\frac{\mathrm{d[NCO]}}{\mathrm{d}t} = -k[\mathrm{NCO}]^a[\mathrm{OH}]^b \tag{1}$$

$$k = k_1 + k_2 = A_1\mathrm{e}^{-E_{\mathrm{a1}}/RT} + [\mathrm{Cat.}]^c A_2\mathrm{e}^{-E_{\mathrm{a2}}/RT} \tag{2}$$

where catalyst dependence is lumped into the rate constant [6–11]. In Eq. (1), k is the rate constant and [NCO] and [OH] are the concentrations of isocyanate and active hydrogen bearing compounds, respectively. Similarly, the exponents a and b represent the order of reaction with respect to isocyanate and active hydrogen bearing compounds, respectively. In Eq. (2), k is expressed with Arrhenius type temperature dependence where A is a frequency factor, E_a is activation energy, R is the universal gas constant, and T is temperature in Kelvin. In addition, [Cat.] is catalyst concentration, c is the order of the reaction with respect to catalyst, and the subscripts 1 and 2 refer to the uncatalyzed and catalyzed components of the reaction, respectively. If no catalyst is used, k is simply represented by the first term in Eq. (2).

If we assume the urethane reaction is run at equal stoichiometry (i.e. [C]=[NCO]=[OH]) and express concentration in terms of conversion (i.e. $[\mathrm{C}]=[\mathrm{C}]_0(1-\alpha)$), Eq. (1) can be rewritten as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k[\mathrm{C}]_0^{n-1}(1-\alpha)^n \tag{3}$$

where $[\mathrm{C}]_0$ is equal to initial isocyanate or active hydrogen bearing compound concentration and $n=a+b$ is the overall order of reaction.

In this study, TPU conversion versus polymerization time data were extracted from the corresponding isothermal DSC time scan through application of the proper energy balance. Detailed procedures describing how these calculations were made have been reported elsewhere [5,12]. The symbols in Figs. 1 and 2 show conversion versus polymerization time profiles of TPU polymerized in the bulk at various temperatures and T31 concentrations for 30 min. As expected, higher polymerization temperatures and T31 concentrations result in higher conversion rates and final conversions after 30 min of polymerization time. In addition to functioning as a thermal stabilizer for PVC, Fig. 2 shows that T31 functions as a powerful catalyst for TPU polymerization. A tin mercaptide, T31 is quite electrophilic and very similar in structure to the commonly used tin carboxylate TPU catalyst, dibutyltin dilaurate.

In order to calculate kinetic parameters for this TPU formulation polymerized at different temperatures and T31 concentrations, the data in Figs. 1 and 2 were fitted to the kinetic rate law model described by Eqs. (2) and (3) with least squares linear regression techniques. To determine the kinetic parameters k and n, log–log plots of $\mathrm{d}\alpha/\mathrm{d}t$ versus $(1-\alpha)$ were constructed from the conversion data in Figs. 1 and 2. Prior to conversions of approximately 0.75–0.99 (depending on polymerization temperature and T31 concentration), these curves were linear within experimental error and had slopes equal to n and y-intercepts equal to $\log\{k[\mathrm{C}]_0^{n-1}\}$. The linear portion of each curve was fitted with a regression line and a value of n and k was calculated. Regardless of polymerization temperature or T31 concentration, an overall order of reaction of 1.7 afforded the best fit to all the data and is used exclusively in all future calculations.

Next, values of k from the linear regression analysis for uncatalyzed TPU reactant mixtures polymerized at different temperatures were used to calculate Arrhenius kinetic parameters for the uncatalyzed component in Eq. (2). Note that in the absence of catalyst the second term in Eq. (2) equals zero and $k=k_1$. Assuming the given kinetic rate law model is valid and n remains constant throughout the entire reaction, a semi-ln plot of k_1 versus $1/T$ should yield a straight line with slope equal to $-E_{\mathrm{a1}}/R$ and y-intercept equal to $\ln[A_1]$. Indeed, as shown in Fig. 3, values of k_1 obtained from the data do form a linear curve when plotted against $1/T$. The Arrhenius parameters A_1 and E_{a1}/R were evaluated from the least squares linear regression line also shown in Fig. 3.

Once Arrhenius kinetic parameters for the uncatalyzed component in Eq. (2) were calculated, values of k obtained from the regression analysis for TPU reactant mixtures polymerized at different temperatures with 0.00688 wt% T31 were used to calculate Arrhenius kinetic parameters for the catalyzed component in Eq. (2). Note that with knowledge of k_1, k_2 can be calculated from $k_2=k-k_1$. Therefore, a semi-ln plot of k_2 versus $1/T$ should yield a straight line with slope equal to $-E_{\mathrm{a2}}/R$ and y-intercept equal to $\ln\{[\mathrm{Cat.}]^c A_2\}$. Indeed, as shown in Fig. 3, values of k_2 do form a linear curve when plotted versus $1/T$. The kinetic parameters $[\mathrm{Cat.}]^c A_2$ and E_{a2}/R were evaluated from the least squares linear regression line shown in Fig. 3. Unfortunately, the Arrhenius parameter A_2 cannot be evaluated without knowing c and was not calculated in this step of the analysis.

Finally, once E_{a2}/R for the catalyzed component in Eq. (2) was calculated, values of k obtained from the regression analysis for TPU reactant mixtures polymerized at 120 °C with different T31 concentrations were used to calculate the remaining kinetic parameters for the catalyzed component in Eq. (2). Here, a log–log plot of k_2 versus [Cat.] should yield a straight line with slope equal to c and y-intercept equal to $\log[A_2\mathrm{e}^{-E_{\mathrm{a2}}/RT}]$. Indeed, as shown in Fig. 4, values of k_2 do form a linear curve when plotted versus [Cat.]. The kinetic parameters $A_2\mathrm{e}^{-E/RT}_{\mathrm{a2}}$ and c were evaluated from the least squares linear regression line shown in Fig. 4. Since,

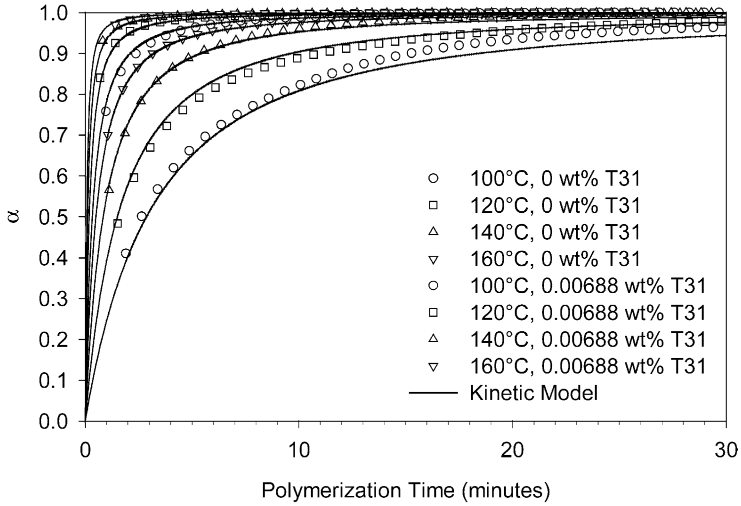

Fig. 1. Experimental and predicted isothermal DSC conversion versus time profiles for uncatalyzed and 0.00688 wt% T31 catalyzed TPU reactant mixtures polymerized at different temperatures.

E_{a2} was already calculated in the preceding analysis step, A_2 was evaluated from $A_2 e^{-E_{a2}/RT}$.

The kinetic parameters evaluated for this TPU formulation compare well to literature values [7,10,11,13–18]. Using these kinetic parameters with Eqs. (2) and (3), the rate law model representing the polymerization kinetics of this TPU formulation can be expressed in terms of conversion as

$$\frac{d\alpha}{dt} = (9.9 \times 10^2 e^{-4700/T} + [\mathrm{wt\%T31}]^{0.89} 1.8 \times 10^5 e^{-4200/T})[C]_0^{0.70}[1-\alpha]^{1.7} \quad (4)$$

where $[C]_0$ equals 1.57 mol NCO/kg TPU solution. This expression is only valid at equal stoichiometry and the rate constant represents contributions from both the uncatalyzed and catalyzed components of the TPU polymerization reaction. This kinetic model can be used to predict the experimental fractional conversion versus time profiles shown in Figs. 1 and 2. Model predictions (solid lines) agree quite well with experimental data over a wide range of polymerization temperatures and T31 concentrations.

3.2. Reaction kinetics of TPU polymerization in situ with PVC

3.2.1. Chemical controlled conversion regime

The symbols in Figs. 5–7 show conversion versus polymerization time profiles of TPU polymerized in situ with PVC at various temperatures, PVC/TPU reactant mixture compositions, and T31 concentrations for 30 min. Note that T31 is introduced as a stabilizer for PVC, but also functions as a catalyst for TPU polymerization. Generally, higher polymerization temperatures, smaller PVC compositions, and larger T31 concentrations result in higher

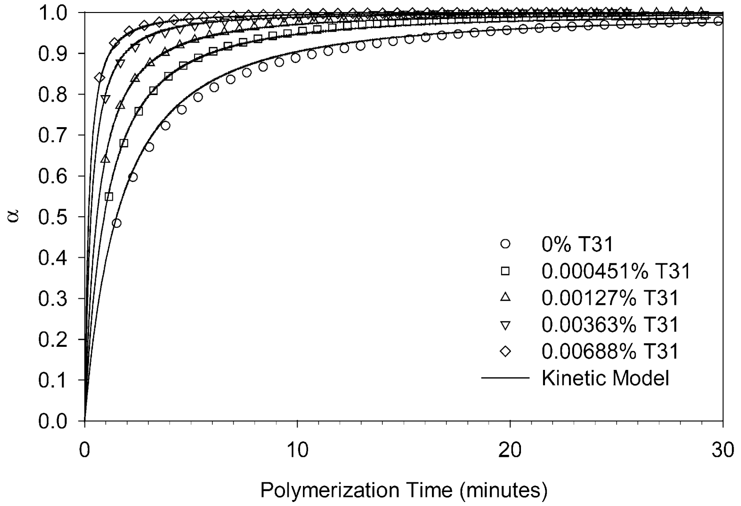

Fig. 2. Experimental and predicted isothermal DSC conversion versus time profiles for TPU reactant mixtures polymerized at 120 °C with different T31 concentrations.

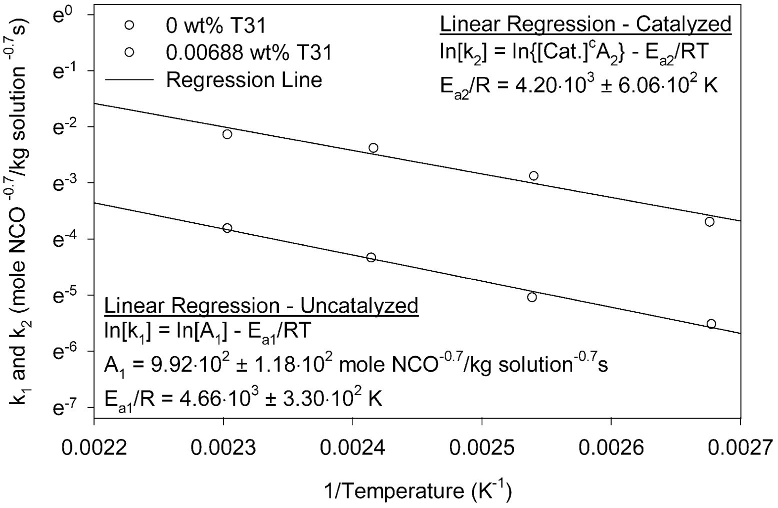

Fig. 3. Evaluation of A_1, E_{a1}/R, and E_{a2}/R from semi-ln plot of DSC k_1 and k_2 versus $1/T$ data for uncatalyzed and 0.00688 wt% T31 catalyzed TPU reactant mixtures polymerized at different temperatures.

conversion rates and final conversions after 30 min of polymerization time. When compared to the data for neat TPU polymerization shown in Figs. 1 and 2 under the same conditions, many of the conversion versus time profiles shown in Figs. 5–7 indicate that TPU conversion rates increase in the presence of PVC. This effect is observed in lieu of the dilutional effect of PVC. In addition, the presence of T31 appears to have a negligible catalytic effect on TPU conversion rate until relatively large T31 concentrations are employed. This behavior is also in contradiction with the results observed for neat TPU polymerization. Finally, the fact that PVC had more than a dilutional effect on TPU reaction rates implies that PVC/TPU reactant mixtures are initially homogeneous on a local scale (i.e. miscible).

To get a better picture of what effect PVC may have on the kinetics of TPU polymerization, the data in Figs. 5–7 were fitted to the kinetic rate law model described by Eqs. (2) and (3) with least squares linear regression techniques. To determine the kinetic parameters k and n, log–log plots of $d\alpha/dt$ versus $(1-\alpha)$ were constructed from the experimental data shown in Figs. 5–7. Note that the kinetic parameters k and n were not determined for the 0.0586 wt% T31 catalyzed PVC/TPU = 44/56 wt% reactant mixture polymerized at 120 °C since this sample practically reached full conversion before DSC kinetic measurements were even made. Prior to conversions of approximately 0.80–0.97 (depending on polymerization temperature, PVC/TPU reactant mixture composition, and T31 concentration), these curves were linear within experimental error and had slopes equal to n and y-intercepts equal to $\log\{k[\mathrm{C}]_0^{n-1}\}$. The linear portion of each curve was fitted with a regression line and a value of n and k was calculated. Identical to the results obtained for neat TPU polymerization, an overall

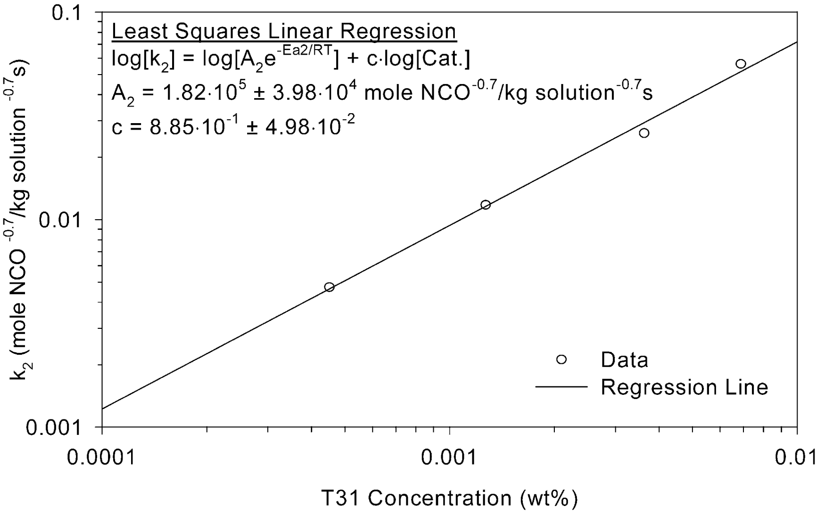

Fig. 4. Evaluation of A_2 and c from log–log plot of DSC k_2 versus T31 concentration data for TPU reactant mixtures polymerized at 120 °C with different T31 concentrations.

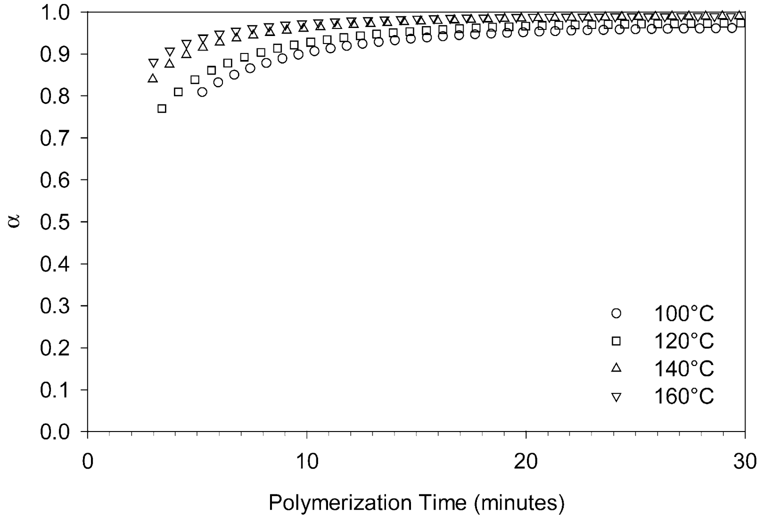

Fig. 5. Experimental isothermal DSC conversion versus time profiles for uncatalyzed PVC/TPU = 44/56 wt% reactant mixtures polymerized at different temperatures.

order of reaction of 1.7 offered the best fit to all the data and is used exclusively in all future calculations.

It should be noted that in the above linear regression analysis, only the Arrhenius controlled conversion regime (i.e. linear portion) of the curves were fitted with a regression line. Past a critical conversion which increased with polymerization temperature, TPU composition, and T31 concentration, the data for each trial became non-linear and thus deviated from the kinetic rate law model set forth in Eqs. (2) and (3). Therefore, only data prior to a particular critical conversion was used in the regression analysis for each curve.

Thus far, it can be concluded that TPU polymerization in situ with PVC obeys the same nth order, phenomenological kinetic rate law model followed by neat TPU polymerization. The overall order of reaction is also the same and equals 1.7 in both cases. Therefore, differences in reaction rate observed between TPU polymerization in situ with PVC and neat TPU polymerization must stem from differences in the overall rate constant, k. To elucidate the dependence of k on PVC, Figs. 8–10 show plots of k versus fractional conversion constructed from the data in Figs. 5–7. Values of k were calculated with Eq. (3) assuming $n = 1.7$. If the TPU polymerization reaction behaved ideally, k would remain constant over the entire range of conversion. In fact, however, k remains relatively constant until a critical value of conversion, α_c, is reached whereby k decreases rapidly to zero. Note that α_c for each plot in Figs. 8–10 is indicated with an arrow. At conversions larger then α_c, k becomes temperature and conversion dependent and thus an Arrhenius type rate constant is no longer applicable. It is believed that such behavior is a consequence of TPU hard segment phase separation from the PVC/TPU reactant mixture, but this topic will be discussed later.

Only considering data prior to α_c, the effect of polymerizaton temperature on k is shown for uncatalyzed

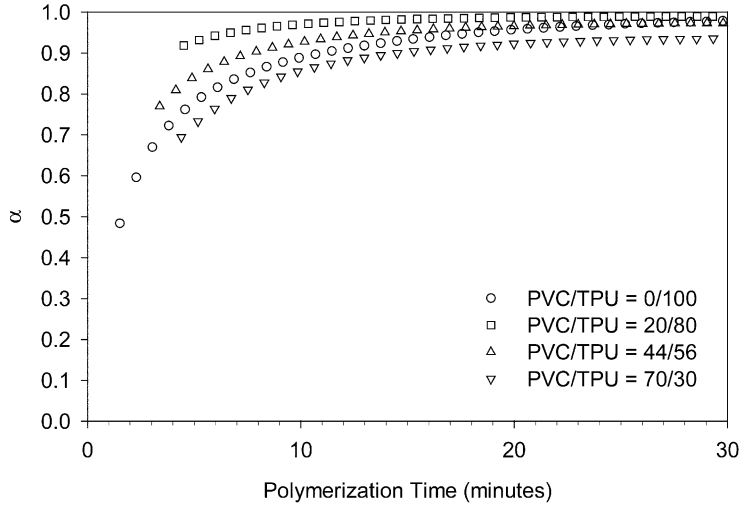

Fig. 6. Experimental isothermal DSC conversion versus time profiles for different uncatalyzed PVC/TPU reactant mixture compositions polymerized at 120 °C.

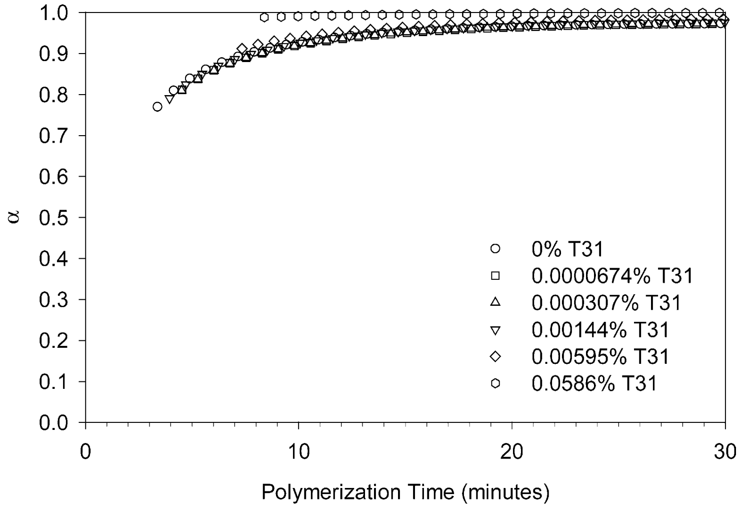

Fig. 7. Experimental isothermal DSC conversion versus time profiles for PVC/TPU = 44/56 wt% reactant mixtures polymerized at 120 °C with different T31 concentrations.

PVC/TPU = 44/56 wt% reactant mixtures in Fig. 8. Naturally, k increases monotonically with polymerization temperature, however, all values of k are still larger than that of uncatalyzed TPU reactant mixtures polymerized at analogous temperatures. In Fig. 9, the effect of PVC composition on k is shown for different uncatalyzed PVC/TPU reactant mixture compositions polymerized at 120 °C. Here, k decreases monotonically with PVC composition, however, all values of k are still larger than that of the uncatalyzed TPU reactant mixture polymerized at 120 °C (taken from Fig. 1). This behavior suggests that k has a dual dependence on PVC composition. Finally, Fig. 10 shows the effect of T31 concentration on k for PVC/TPU = 44/56 wt% reactant mixtures polymerized at 120 °C. This figure reveals that T31 concentration has little effect on k until relatively high concentrations of 0.00595 wt% are reached. This is in contrast to the results obtained for catalyzed TPU reactant mixtures polymerized at 120 °C where T31 concentrations as low as 0.000451 wt% had a dramatic effect on k (Fig. 4). This behavior suggests that the presence of PVC eliminates the catalytic effect of T31 on TPU polymerization until relatively high T31 concentrations are reached.

To understand the dependence of k on PVC composition, any catalytic effect of PVC on the TPU polymerization reaction was considered. Commercial suspension polymerized PVC homopolymer formulations produced by US manufacturers using large reactors are far from pure. Typical resins contain residual vinyl chloride, water, initiator fragments, suspending agents, and buffer salts as impurities [19]. In communication with Mr Ronald Davis of the Oxy Vinyls company [20], it was also discovered that the ester peroxide initiated PVC homopolymer used in this study contained phenolic antioxidant and organic monolaurate antistatic additives. It is quite likely that one or a combination of these impurities and additives catalyze the TPU polymerization reaction. That would explain why the

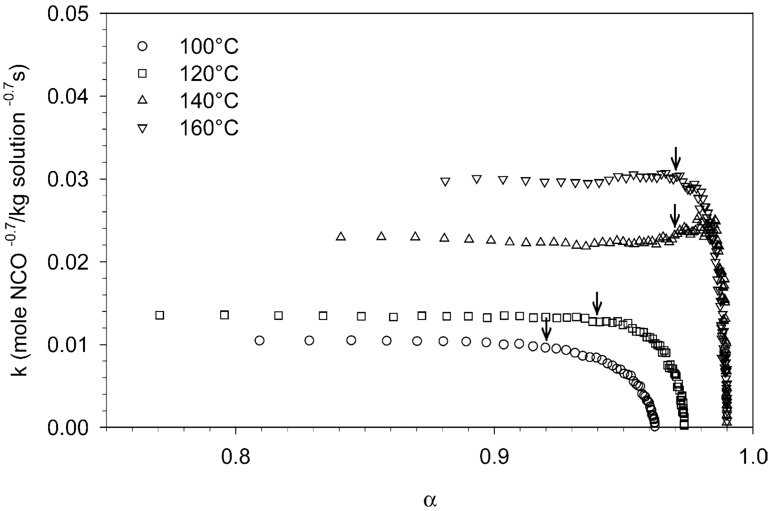

Fig. 8. Plots of DSC k versus conversion for uncatalyzed PVC/TPU = 44/56 wt% reactant mixtures polymerized at different temperatures.

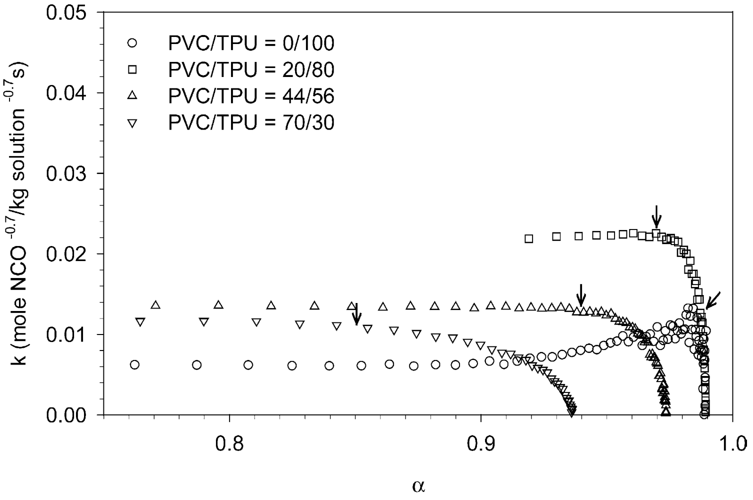

Fig. 9. Plots of DSC *k* versus conversion for different uncatalyzed PVC/TPU reactant mixture compositions polymerized at 120 °C.

values of *k* for TPU polymerization in situ with PVC (at all PVC compositions) in Figs. 8 and 9 are larger than values of *k* observed for neat TPU polymerization at analogous polymerization temperatures. However, if this were the only additional mechanism leading to higher rates of TPU polymerization, the values of *k* obtained for TPU polymerization in situ with PVC would not decrease with PVC composition. Instead, they would increase with PVC composition, and thus PVC impurity/additive concentration. Similarly, introducing another rate constant to account for the catalytic TPU polymerization reaction that occurs in the presence of various PVC additives does not explain the lack of *k* dependence on T31 concentration as shown in Fig. 10.

In the preparation of PVC/TPU reactant mixtures for these kinetic studies, PVC was completely unstabilized or was stabilized with very low T31 concentrations. Consequently, even though a relatively low mixing temperature of 120 °C was used to prepare these reactant mixtures, some dehydrochlorination was likely during sample preparation and kinetic analysis. As proof of PVC dehydrochlorination, Fig. 11 shows partial Raman spectra of an unstabilized PVC/TPU = 44/56 wt% reactant mixture after 1, 30 min, and 2 h of polymerization at 120 °C. After 30 min of polymerization time, two new bands appear at Raman shifts of 1100 cm^{-1} and 1480 cm^{-1}. Quite large after 2 h of polymerization time, these bands originate from conjugated polyene stretching vibrations in the backbone of PVC that are produced as a result of dehydrochlorination [21,22].

It is well known that the dehydrochlorination of PVC results in the elimination of hydrogen chloride (HCl). Hence, it is probable that TPU polymerization in situ with PVC occurs in a finite concentration of HCl, especially if PVC is unstabilized. From the patent literature it is known that organic acyl halides will inhibit the polymerization of isocyanates with themselves over extended periods of time [23]. Typical examples of acyl halides include acetyl chloride, fumaryl chloride, propionyl chloride, succinyl

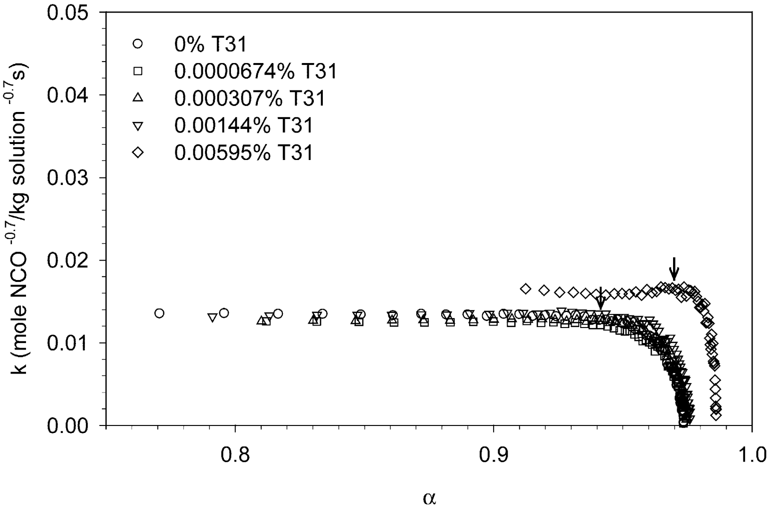

Fig. 10. Plots of DSC *k* versus conversion for PVC/TPU = 44/56 wt% reactant mixtures polymerized at 120 °C with different T31 concentrations.

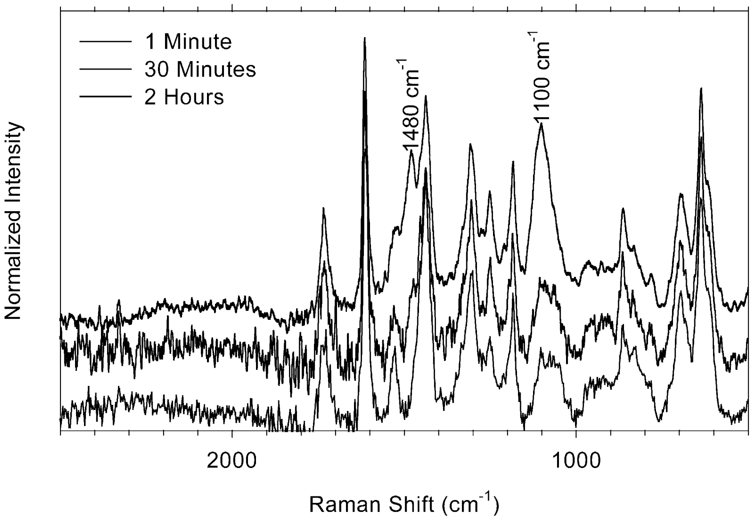

Fig. 11. Raman spectra of an unstabilized PVC/TPU = 44/56 wt% reactant mixture after 1, 30 min, and 2 h of polymerization at 120 °C.

chloride, and benzoyl chloride. Other compounds such as phosphorus trichloride, phosphorus pentachloride, and phosphorus oxychloride have been shown to function in the same way [24]. Other studies have shown that strong acids such as HCl have a strong inhibiting effect on the kinetics of alkyltin carboxylate catalyzed urethane reactions [25–27].

If the impurities/additives in PVC can function as TPU polymerization catalysts as discussed earlier, the same inhibiting effect caused by PVC dehydrochlorination would cause k to decrease with increasing PVC composition and thus evolved HCl concentration. Hence, it is believed that both the catalytic impurities/additives and inhibiting HCl in PVC are responsible for the dependence of k on PVC composition shown in Fig. 9. At low PVC compositions, it is believed that impurities/additives in PVC catalyze TPU polymerization and k increases. However, after some critical PVC composition is reached ((20 wt%), the inhibiting influence of HCl becomes dominant and k begins to decrease. The inhibiting effect of HCl is also responsible for the dependence of k on T31 concentration shown in Fig. 10. At any one time, T31 is both stabilizing PVC and converting HCl to an innocuous state, or it is catalyzing the TPU polymerization reaction. Agents able to share the catalyst should slow the TPU polymerization reaction. Therefore, the dehydrochlorination of PVC and the presence of HCl will neutralize a finite quantity of T31 catalyst, thereby slowing the measured rate of TPU polymerization in situ with PVC. This effect is observed in Fig. 10 where k is relatively independent of T31 concentration until some critical concentration is reached.

Next, an effort was made to model the kinetics of TPU polymerization in situ with PVC in the absence of T31. The kinetic rate law model depicted in Eq. (3) with $n = 1.7$ can be used for this purpose, but an expression for k still needs to be developed. If k is a function of temperature and PVC composition, k can be expressed as

$$k = k_1 + k_3 = A_1 e^{-E_{a1}/RT} + k_3(T, \phi) \qquad (5)$$

where subscript 1 refers to the uncatalyzed component of the reaction, subscript 3 refers to the catalyzed/inhibited component of the reaction that occurs in the presence of PVC, and ϕ denotes PVC composition.

With Eq. (5) in mind, values of k for different PVC/TPU reactant mixture compositions polymerized at 120 °C were used to calculate values of k_3 for each PVC composition. Note that with knowledge of k_1 (Section 3.1), k_3 can be calculated from $k_3 = k - k_1$. Plotted in Fig. 12, k_3 decreases with increasing PVC composition. This behavior is consistent with the idea that HCl eliminated during PVC dehydrochlorination inhibits the rate of TPU polymerization in situ with PVC. However, the fact that k_3 must equal zero in the absence of PVC indicates the need for an additional rate constant to fully account for the dependence of k on PVC composition. Fully modeling the dependence of k on PVC is beyond the scope of this study and will not be investigated further here.

3.2.2. *Diffusion controlled conversion regime*

After investigating and partially modeling the kinetics of TPU polymerization in situ with PVC in the conversion regime below α_c, we will now turn our attention to the conversion regime above α_c. As shown in Figs. 8–10, k remains constant until some critical conversion is reached, whereby k decreases with conversion and rapidly approaches zero. Generally, α_c decreases with decreasing polymerization temperature, increasing PVC composition, and decreasing T31 concentration. It is believed that such behavior is a consequence of TPU hard segment (HS) phase separation from the PVC/TPU reactant mixture.

To understand why, the process of neat TPU HS phase separation and domain ordering must be understood. As a TPU polymerization reaction proceeds, an increase in molecular weight ultimately leads to some degree of soft

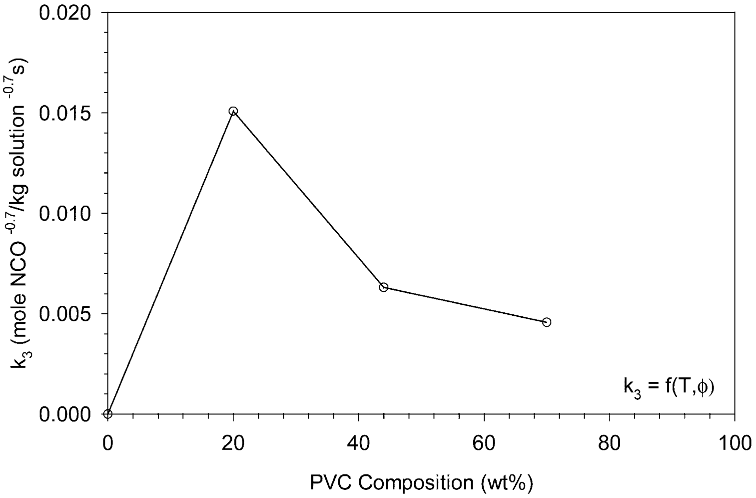

Fig. 12. Plot of DSC k_3 versus PVC composition for different uncatalyzed PVC/TPU reactant mixture compositions polymerized at 120 °C.

segment/hard segment thermodynamic immiscibility. A progressive phenomenon, phase separation leads to domain formation as conversions approach unity. Due to their relatively high T_g and crystallinity, HS rich domains 'physically cross-link' the TPU reactant mixture leading to a drastic reduction in reactant mobility and the apparent rate constant. When this occurs, the overall rate of reaction is no longer controlled by chemical reactivity and the kinetics become diffusion controlled [28–30,31].

For the neat TPU investigated in this study, this process occurs at conversions close to unity. However, as shown in Figs. 8–10, when TPU is polymerized in situ with PVC, TPU HS phase separation begins at lower conversions as manifested by a decrease in α_c. Assuming PVC/TPU reactant mixtures are initially homogeneous on a molecular scale, PVC appears to enhance the thermodynamic drive for TPU HS phase separation. In support of this, many of the DSC temperature scans used to measure ΔH_r (Ref. [12]), and thus calculate the data shown in Figs. 5–7, displayed a single endothermic peak at temperatures of 120–145 °C. Discussed in more detail elsewhere [5], this endotherm was attributed to the disruption of short range and/or long range non-crystalline HS domain ordering in the PVC/TPU reactant mixture. An analogous endotherm was not observed for neat TPU.

It is interesting to note that in Fig. 10, increasing T31 concentration leads to a higher α_c (and molecular weight) before TPU HS phase separation occurs. An analogy occurs in highly phase separated polyether based TPUs where low levels of catalyst lead to premature phase separation, low molecular weight, and poor physical properties. Not shown here, the same phenomenon was observed for the lower T31 concentrations in Fig. 10.

To obtain a better picture of what effect TPU HS phase separation has on the conversion regime above α_c, master curves of conversion versus polymerization time were constructed by multiplying the abscissa data in Figs. 5–7 with a factor, A, such that the conversion regimes less than α_c in all curves are superimposed at a given reference state. The reference state chosen for each figure was that of an uncatalyzed (T31) PVC/TPU = 44/56 wt% reactant mixture polymerized at 120 °C. Shown in Figs. 13–15, the superposition of individual curves is quite good in the chemically controlled conversion region below the α_c for each curve (indicated with arrows). However, in the diffusion controlled region above the α_c for each curve, the data branches off the master curve and appears to level off at some limiting conversion. The physical meaning of all conversion versus polymerization time data reducing to a single curve in the chemically controlled portion of the TPU polymerization reaction is that the reaction mechanism was the same, irrespective of polymerization temperature, PVC/TPU composition, and T31 concentration. Therefore, the values of A used in constructing Figs. 13–15 simply reflect the value of k at different polymerization temperatures, PVC/TPU compositions, and T31 concentrations. The physical meaning of the data for a given set of polymerization conditions branching off the master curve at some α_c in the diffusion controlled portion of TPU polymerization is that k becomes conversion dependent when TPU HS phase separation and domain ordering begin.

4. Conclusions

TPU polymerization in situ with PVC was accompanied by TPU HS phase separation and domain ordering prior to full conversion. This was in contrast to neat TPU polymerization where HS phase separation and domain ordering occurred at conversions close to unity. Hence, the presence of PVC appeared to enhance the thermodynamic drive for TPU HS phase separation from the PVC/TPU reactant mixture. It is also probable that TPU HS phase separation is simply a prelude to PVC/TPU blend phase

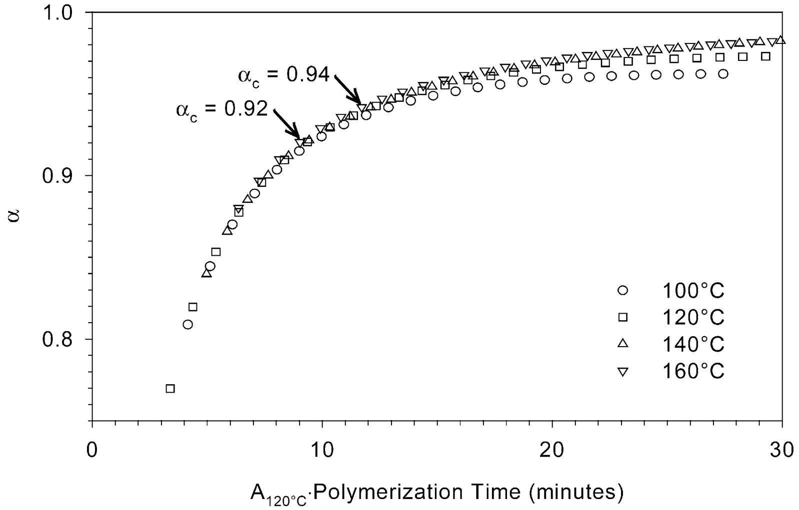

Fig. 13. Master curve of experimental isothermal DSC conversion versus time data for uncatalyzed PVC/TPU = 44/56 wt% reactant mixtures polymerized at different temperatures (reference polymerization temperature of 120 °C).

separation in general, as this blend system has been shown to be partially miscible at high TPU molecular weight [5].

Prior to HS phase separation, and thus some critical conversion, TPU polymerization in situ with PVC obeyed the same nth order, phenomenological kinetic rate law followed by neat TPU polymerization. However, the overall rate constant employed in the rate law, and thus the rate of TPU polymerization, increased in the presence of unstabilized PVC. It is believed that some of the impurities and additives in the suspension polymerized PVC catalyzed TPU polymerization. However, while the overall rate constant was greater than that for neat TPU polymerization, it actually decreased with increasing PVC composition. In addition, T31 concentration had little effect on the overall rate constant until relatively high concentrations were reached. In both cases, TPU polymerization was inhibited by increasing concentrations of HCl liberated during the dehydrochlorination of PVC.

After HS phase separation, and thus some critical conversion, the kinetics of TPU polymerization in situ with PVC were no longer chemically controlled. In this conversion regime, the apparent rate constant of the reaction became both temperature and conversion dependent and rapidly approached zero. Such behavior was speculated to originate from a form of topological overall diffusion control whereby TPU HS phase separation, HS domain ordering, and the resulting physical cross-linking of the PVC/TPU reactant mixture limited TPU reactant mobility. Analogous to chemical gelation, this process of physical gelation drastically slowed the rate of TPU polymerization at high conversions, resulting in limiting conversions.

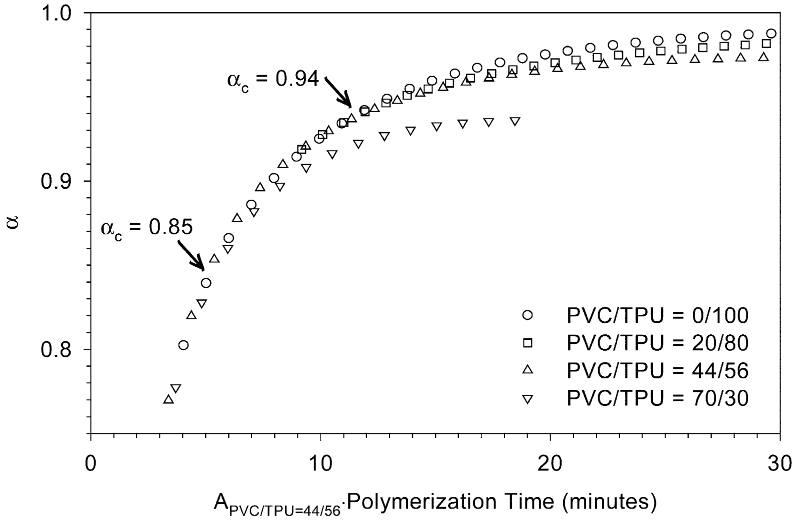

Fig. 14. Master curve of experimental isothermal DSC conversion versus time data for different uncatalyzed PVC/TPU reactant mixture compositions polymerized at 120 °C (reference PVC/TPU composition of 44/56 wt%).

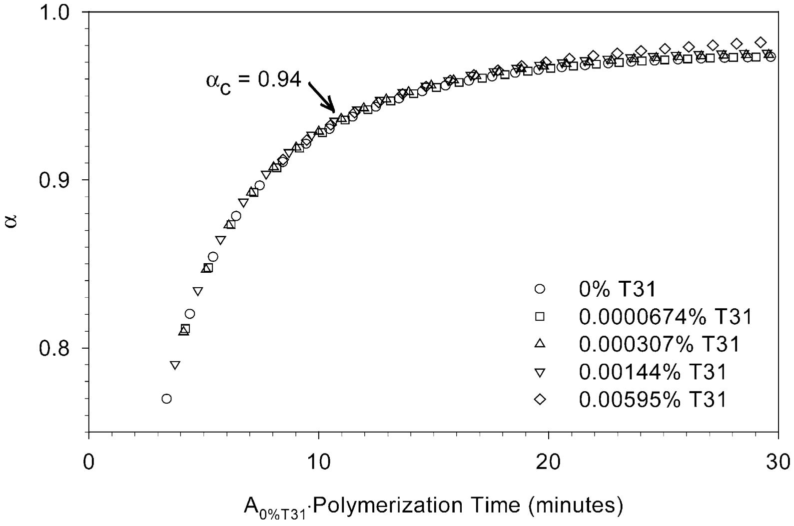

Fig. 15. Master curve of experimental isothermal DSC conversion versus time data for PVC/TPU = 44/56 wt% reactant mixtures polymerized at 120 °C with different T31 concentrations (reference T31 concentration of 0 wt%).

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