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Studies on Cure Chemistry of New Acetylenic Resins

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ABSTRACT: This paper describes cure studies of arylacetylene-terminated resins to gain some fundamental understanding of the influence of various structural aspects of a molecule on its cure chemistry. Of particular interest are the effects of the number of acetylenic substituents on the aromatic ring and their relative positions to one another. Activation energy (*E*) of the cure reaction as calculated from dynamic DSC analysis reveals that there is a direct correlation between the activation energy and the stability of radicals formed by thermal initiation. Based on model compound studies, it is evident that the resonance stabilization of radicals contributes significantly to the lowering of activation energy values. When the number of substituents on the aromatic ring varies, the combined influence of resonance, inductive, proximity, and steric factors needs to be considered. Studies with blends of acetylenic monomers suggest that the possible chain-initiating species are those radicals which can be stabilized by resonance. From the DSC data, we also infer that the radicals formed initially may not be very selective in the reaction with other multiple bonds in their vicinity.

Introduction

The chemistry of resins with terminal acetylenic groups has witnessed a very rapid development in the past two decades. The impetus for research in this direction is the fact that these resins cure via an addition reaction as a consequence of which no volatile byproducts are evolved during the processing stage. In addition to maintaining the processing ease, they afford cured products that have high thermal stability and good mechanical properties. Hence, much effort has been focused on using these resins as matrices for high-performance, fiber-reinforced composites. Furthermore, their high thermal stability also qualifies them as excellent candidates for carbon matrices in carbon/carbon composites.

The goal of this work is to gain some fundamental understanding of the polymerization of acetylenes. The mechanism of polymerization of arylacetylenes has been investigated by several research groups,[1–5] but the complexity of the reaction and the infusible and intractable nature of the cured resins have made analysis very difficult. As part of our ongoing research program on high-temperature materials, several new aryl acetylenic monomers have been synthesized.[6–9] Herein, we have studied the cure reaction of a family of such monomers which differ from one another slightly in their structural characteristics. By varying the number of acetylenic groups substituted on the benzene ring as well as their relative position, we have made an attempt to derive some insight into the influence of resonance, steric, inductive, and proximity effects on the cure reaction mechanism. Toward this goal, some model compounds have also been synthesized and studied.

The target compounds chosen for this study are three arylacetylenic systems. Two of these are trisubstituted with the acetylenic substituents at the 1,2,4 and 1,3,5 positions, and the other is a tetrasubstituted analog with the acetylenic substituents at the 1,2,4,5 positions. The detailed synthesis of these compounds, their cure conditions, and their thermal stabilities have been reported.[9,10] To rationalize the cure reaction data obtained for these compounds, it was necessary to obtain similar data on simpler disubstituted compounds. For instance, the contribution of resonance stabilization toward the activation energy may be unambiguously established by comparing the data of either the 1,2 or 1,4 disubstituted compound with that of the 1,3 isomer. While additional stabilization of the radical species is possible via phenylethynyl substituents attached at the ortho or para positions, a meta isomer is incapable of providing this delocalization. This kind of information may be very helpful in understanding the influence of various structural aspects of the molecule on its cure chemistry and also aid in the molecular design of new materials. The compounds used in this study have a common feature in the sense that they all have phenylethynyl groups appended to a benzene ring. Their chemical structure and the substitution pattern on the benzene ring, by which they will be referred to hereafter, are presented in Table I.

Theory

The objective in characterizing the cure of a thermoset is to obtain a complete description of curing that is commensurate with its ultimate use. The generation of accurate time–temperature–degree of conversion curves is of great practical importance for establishing optimum cure schedules. From a mechanistic point of view, evaluation of the activation energy of the cure reaction can give valuable information on barriers to reaction and mechanisms. The dynamic DSC method, used in this study to obtain the activation energy (*E*), capitalizes on the variation in peak exotherm temperature (T_p) with the heating rate (ϕ). A simple relationship between activation energy, heating rate, and peak exotherm temperature is based on the work of Ozawa.[11,12] In general, the basic rate equation relates the extent of conversion ($d\alpha/dt$) at constant temperature to some function of the concentration of the reactants, $f(\alpha)$, through a rate constant k:

$$d\alpha/dt = kf(\alpha) \tag{1}$$

The temperature dependence is assumed to reside in the rate constant through an Arrhenius relationship given by

$$k = Ae^{-(E/RT)} \tag{2}$$

Combining the two equations,

$$d\alpha/dt = f(\alpha)Ae^{-(E/RT)} \tag{3}$$

Integration of this equation proceeds as follows:

$$\int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = A\int_{t_0}^{t_p} e^{-(E/RT)}\,dt \tag{4}$$

If the temperature is raised at a fixed rate ϕ, then the integration limits t and t_0 can be changed to T and T_0,

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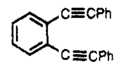
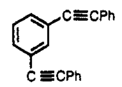
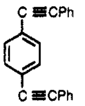
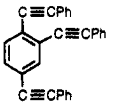
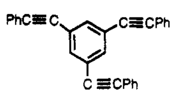
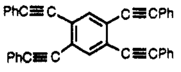
Table I. Molecular Structures of the Various Compounds Used in This Study Showing the Substitution Pattern by Which They Will Be Referred To

STRUCTURE	REFERRED TO AS
	12
	13
	14
	124
	135
	1245

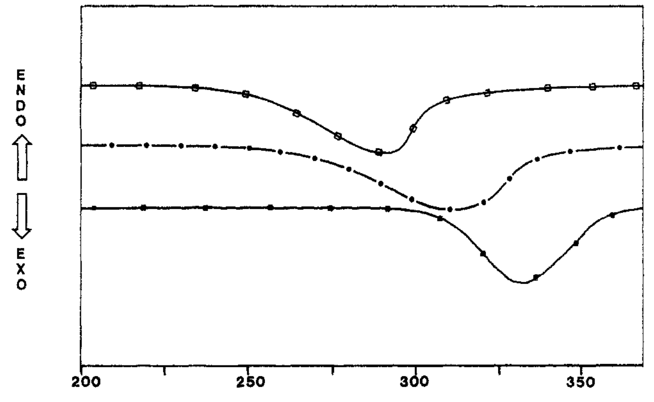


Figure 1. DSC scans showing the cure exotherm of **1245** (□), **124** (●), and **135** (■).

respectively. Furthermore, if the reaction rate is assumed to be low at low temperature (which is very reasonable as resins involved in the present study are capable of curing only at high temperatures), then the next approximation yields

$$\int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \int_{T_0}^{T_p} e^{-(E/RT)}\, dT = \frac{A}{\phi} \int_0^{T_p} e^{-(E/RT)}\, dT \qquad (5)$$

The value of the right side of eq 5 is expressed in terms of $p(E/RT)$ and is tabulated by Doyle[13,14] for the commonly encountered range of $20 < (E/RT) < 60$, as the following function (eq 7):

$$\frac{A}{\phi} \int_0^{T_p} e^{-(E/RT)}\, dT = \frac{AE}{\phi R} p(E/RT) \qquad (6)$$

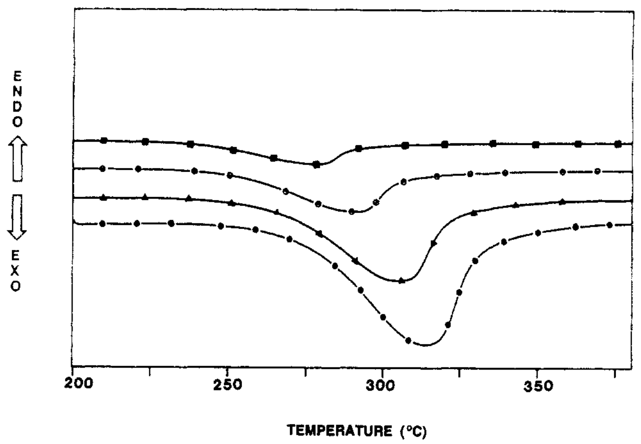


Figure 2. DSC scans of **1245** obtained at a heating rate of 5 (■), 10 (O), 20 (▲), and 30 °C/min (●).

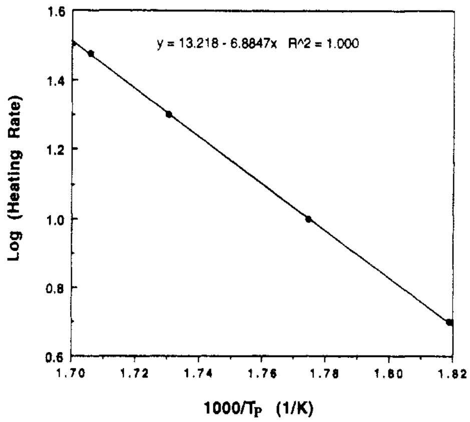


Figure 3. Plot of log(heating rate) vs $1/T_p$ for **1245**.

$$\log p(E/RT) = -2.315 - 0.4567(E/RT) \qquad (7)$$

As a general rule for thermoset cure reaction, it has been observed[15-17] that the extent of reaction at the peak exotherm, α_p, is constant and independent of the heating rate.

$$\int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{AE}{\phi_1 R} p(E/RT_{p_1}) = \frac{AE}{\phi_2 R} p(E/RT_{p_2}) \qquad (8)$$

$$E = \frac{-R}{0.4567} \frac{\Delta \log \phi}{\Delta(1/T_p)} \qquad (9)$$

From the peak reaction temperatures as a function of heating rate, the activation energy can be calculated with a precision of 2–3%.[18]

Experimental Section

1245, **124**, and **135** were synthesized from the corresponding bromobenzenes and phenylacetylene in the presence of activated Pd catalyst.[9,10] The disubstituted isomers were also synthesized in an analogous manner to serve as model compounds. DSC scans were run on a Perkin-Elmer 7700 thermal analysis system equipped with a differential scanning calorimeter (DSC7). For our studies, 3–5 mg of sample weight, an inert atmosphere of nitrogen, and heating rates of 5, 10, 20, and 30 °C/min were employed for the dynamic DSC experiments. Blends of **1245** with **135** or diphenylacetylene with various compositions were made by dissolving the various components in methylene chloride and evaporating off the solvent.

Results and Discussion

Results of the DSC studies are presented in Figures 1–6. DSC scans revealing the cure exotherms of **1245**, **124**, and **135** at a heating rate of 10 °C/min are shown in

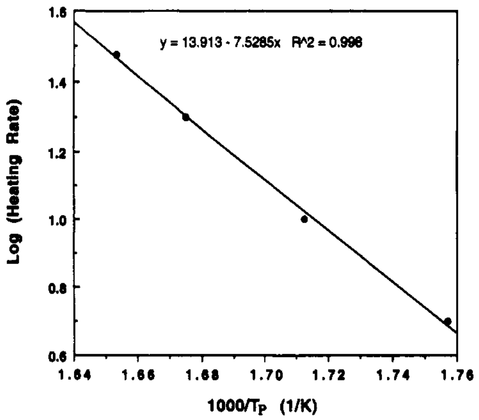


Figure 4. Plot of log(heating rate) vs $1/T_p$ for **124**.

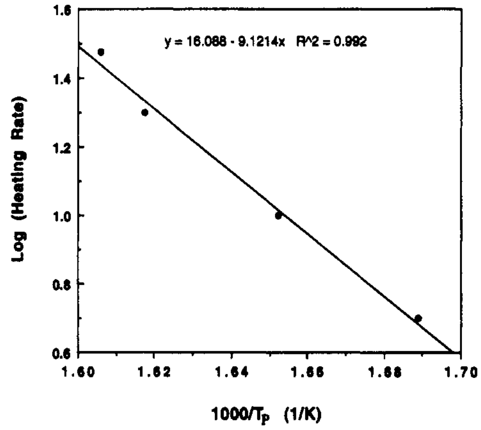


Figure 5. Plot of log(heating rate) vs $1/T_p$ for **135**.

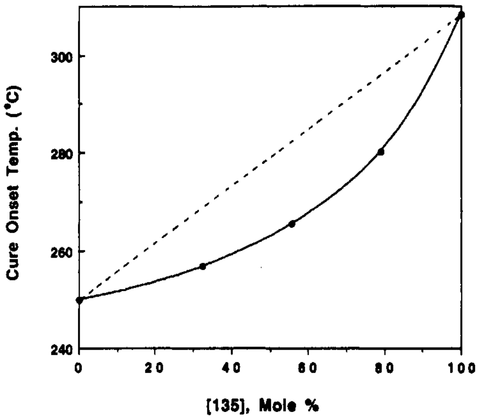


Figure 6. Plot of cure onset temperature vs composition for the **1245**/**135** blend system.

Table II. Activation Energy Data for the Cure Reaction of Various Acetylenic Compounds Studied

compd	E (kJ/mol, ±2%)	compd	E (kJ/mol, ±2%)
1245	125	**12**	125
124	137	**14**	127
135	166	**13**	140

Figure 1. Their cure onset temperatures, measured as the point of interaction of the extrapolated baseline and the initial steep portion of the curve, are 251, 266, and 308 °C, respectively, and the corresponding peak exotherm temperatures are 291, 311, and 332 °C. One representative plot of shift in peak position as a function of heating rate is shown in Figure 2 for **1245**. Plots of log(heating rate) vs inverse of peak temperature ($1/T_p$) for **1245**, **124**, and **135** are shown in Figures 3, 4, and 5, respectively. Similar plots were obtained for the **12**, **13**, and **14** disubstituted analogs. The activation energy values calculated from the slopes of these plots for all the compounds investigated are presented in Table II. DSC data presented in Figure 6 were obtained for the **1245** and **135** blend system at a heating rate of 10 °C/min.

Kovar et al.,[19] Kern,[20] and Admur et al.[21] have discussed the mechanism of the thermal polymerization of phenylacetylenes with and without radical initiators. In the absence of initiators, in general, the observed polymerizations are predominantly initiated by the thermal homolysis of impurities, including peroxides or hydroperoxides formed due to oxygen, present in the monomer. In fact, most monomers when exhaustively purified do not undergo a purely thermal, self-initiated polymerization in the dark.[22] However, once initiated, a number of reaction routes are possible during the thermal polymerization of acetylenic compounds. For instance, trimerization which yields substituted benzenes, Diels–Alder reaction with the polymer backbone, and linear or branched polymerization to form conjugated linkages are some of the ways by which chain propagation could occur. Calculations based on bond energies for probable routes of polymerization have been reported.[23] The calculated ΔH value for the cyclization of three acetylenic groups is 189 ± 10 kJ/mol. The heat of polymerization, ΔH_p, calculated from the area under the cure exotherm of the disubstituted acetylenic compounds is 231 ± 4 kJ/mol or 115.5 kJ/mol of the acetylenic groups. The calculated ΔH_p for all the compounds investigated here is less than 120 kJ/mol. The fact that the heat of polymerization of these acetylenic compounds is less than the enthalpy of trimerization suggests that trimerization is not the major reaction pathway during initial polymerization. Furthermore, trimerization of these secondary acetylenic groups to form hexasubstituted benzene rings appears to be a sterically unfavorable process. The bulky phenyl moieties linked to the acetylenic groups would probably preclude achievement of the necessary orientation for the trimerization reaction. The likely product formed in the initial stage of polymerization is a branched polyene, which could further undergo a variety of addition reactions to yield a cross-linked polymer.

The activation energies for the thermal cure reaction of **1245**, **124**, and **135** are 125, 137, and 166 kJ/mol, respectively (Table II). An independent check on the accuracy of the measured activation energy was performed by isothermal FTIR studies.[24] The value obtained by the FTIR method is in good agreement with that derived from dynamic DSC studies. Considering the first step in these polymerizations, the initial radical likely to form is the one that could be stabilized by way of resonance. The lower activation energy of the **1245** cure reaction is probably due to the extensive stabilization by resonance that its radicals can realize. The lower activation energy of the compound is reflected in the lower cure onset temperature (251 °C). The difference in the activation energies between **124** and **135** is also presumably due to the resonance effect. While the radical obtained from **124** can be stabilized due to resonance, no such stabilization is possible with the **135** derivative. Further evidence in favor of resonance stabilization of radicals and its influence on activation energy is provided by comparing the data of the disubstituted compounds. The activation energies of **12** and **14** are 125 and 127 kJ/mol, respectively, while that of **13** is 140 kJ/mole. This higher value obtained for **13** relative to **12** and **14** implies that resonance stabilization of the radicals does contribute to the lowering of the activation energy. With **12**, the close proximity of the acetylenic bonds could lead to formation of either five- or six-membered rings.[25,26] On this basis, it was suspected that **12** would have a lower activation energy than **14**. However, the fact that the activation energies of **12** and **14** are almost comparable suggests that the resonance effect outweighs the proximity factor. Comparison of the data obtained when the number of substituents on the benzene ring is different does not seem straightforward. For instance, the activation energy of **13** is 140 kJ/mol while that of **135** is 166 kJ/mol. Since the resonance effect does not come into play in either case and steric and proximity contributions are negligible, the increase in activation energy may be solely due to the inductive effect of the additional group on the benzene ring. In contrast to this set of results, **12** and **1245** have an identical activation energy of 125 kJ/mol. In the case of **1245**, the overwhelming contribution from the resonance effect probably dominates all the other contributing factors. On the whole, these results suggest that the combined effect of resonance, steric, inductive, and proximity factors has to be invoked for rigorous comparison of the cure reaction data.

Studies on blends of **1245** and **135** were carried out to obtain additional information on the stability of the radicals formed and their selectivity in the chain propagation reaction. This system was chosen on the basis that there was no overlap in the cure exotherms (Figure 1) of these two compounds. The DSC scans of the blends show two different melting endotherms but only one cure exotherm for all the compositions studied. Furthermore, the profile of the cure exotherm is similar to those obtained for the pure compounds, i.e., devoid of any shoulder which would suggest the overlap of two different cure peaks. Figure 6 shows the cure onset temperature of the blend as a function of the composition. It is observed that the cure onset temperature is always lower than that predicted by the rule of ideal mixtures shown by the dotted line. A similar trend is observed with the peak temperature of the cure reaction. This lower cure onset temperatures of the blend probably implies that the **1245** is consumed early in the cure reaction. The fact that a second exotherm is not seen may also suggest that the more stable **1245** radicals, once formed, react with themselves as well as with **135** acetylenic bonds. In other words, at the high reaction temperatures that are involved, the radicals are probably not very selective in their reaction with other multiple bonds. Another set of experiments on blends of diphenylacetylene and **1245** affords results similar to those shown in Figure 6. Our earlier attempts to obtain the cure exotherm of pure diphenylacetylene as a model compound were unfruitful, at it has a boiling point of 300 °C at 760 mmHg (the signal in the DSC trace goes off scale around 360 °C). However, blends of **1245** and diphenylacetylene showed cure exotherms below 340 °C, indicating that all of the diphenylacetylene is consumed much before the boiling point of diphenylacetylene is approached. This result lends indirect support to our earlier inference on the inability of the radicals to be selective in the chain propagation reaction.

Conclusion

Activation energies for the cure reaction of various acetylenic monomers have been investigated. Tetrasubstituted **1245** has a lower activation energy compared to trisubstituted **124** and **135**, probably due to greater resonance stabilization that is possible with the **1245** radicals. This resonance stabilization factor can also account for the lower activation energy of **124** compared to **135** and of **12** and **14** compared to **13**. Studies with blends reveal that the cure onset and peak temperatures for all compositions of the blend are lower than that predicted by the rule of ideal mixtures. These results suggest that, first, the more stable radical species are formed and, second, the radicals are not very selective in their reaction with other multiple bonds.

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