

The kinetics of surface craze growth in polycarbonate exposed to normal hydrocarbons

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A variable radius of curvature strain bending apparatus has been used to investigate the propagation of surface crazes in polycarbonate exposed to a series of normal hydrocarbons from *n*-hexane to *n*-dodecane. In all cases it was found that for crazes growing in a zone free of other crazes, the growth rate was linear at constant temperature, and exponentially dependent upon temperature. An activated-state theory was developed to describe the kinetics of growth in terms of two parameters, B , a dimensionless strain constant which was independent of both the test variables and the crazing agent used, and A' a characteristic growth rate parameter that varied exponentially with temperature where $A' = G_0 \exp -\Delta E_G/RT$. The rate constant G_0 and the activation energy ΔE_G correlate with the square of the difference between the solubility parameters of the crazing agent and polycarbonate.

1. Introduction

In an earlier study, Nicolais and DiBenedetto [1] developed a kinetic model to describe the rates of nucleation and growth of crazes on the surface of a homogeneous polymer under stress. More recently, the theory was tested in a study of the kinetics of surface craze growth in polycarbonate exposed to normal heptane [2]. In that study, it was found that for crazes growing in a zone free of other crazes, the growth rate was linear at constant temperature, and exponentially dependent upon temperature. The rate of growth was characterized by two parameters, a dimensionless strain constant, B , which was independent of test variables, and a characteristic growth rate parameter, A , which varied exponentially with temperature. It was also shown that a strain-temperature equivalence principle could be used to predict the crazing behaviour over a range of temperature and strains.

In this work we have extended the study to a range of normal hydrocarbons in order to determine if the kinetic parameters could be correlated

in a simple fashion to the properties of the craze-inducing solvents. We will show that the dimensionless strain parameter, B , is independent of solvent, as well as test variables, and that the growth rate parameter correlates simply with the square of the differences between the solubility parameters for the crazing agents and polycarbonate.

2. Analysis

When a polymeric solid is flexed and the surface under tension is exposed to a solvent, crazes nucleate at the surface at sites of stress inhomogeneity, and, subsequently, grow to macroscopic dimensions in a direction perpendicular to the imposed tensile load. When the distance between crazes is sufficient, the nucleation and growth of a surface craze are not affected by the presence of others. Under such conditions, it has been shown that both the nucleation rate and the growth rate of the "non-interfering" crazes are linear [3, 4] and can be represented by one-dimensional models [5]. In a previous paper, Nicolais and DiBenedetto [1] assumed that the initial nucleation rate and the

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growth rate were activated processes that could be represented by Arrhenius-type equations. Following the lead of Zhurhov *et al.* [4], they used the following rate equations:

$$dN/dt = N_0 \exp(-\Delta E_n/RT) \sinh(n-1)\sigma/\sigma^* \quad (1)$$

where dN/dt is the nucleation rate, N_0 is a constant, E_n is the activation energy for nucleation, R is the gas constant, T is absolute temperature, $(\sigma^*/n-1)$ is a characteristic stress constant, and σ is the maximum imposed tensile stress, and

$$dG/dt = G_0 \exp(-\Delta E_G/RT) \sinh \sigma/\sigma^* \quad (2)$$

where dG/dt is the craze growth rate, G_0 is a constant, ΔE_G is the activation energy for the one-dimensional growth process, and σ^* is a characteristic stress constant.

When the test specimens are exposed to a solvent, craze nucleation occurs and the crazes grow perpendicular to the direction of the applied stress. At constant temperature, Equation 2 may be integrated to give:

$$G(t) = G_0 \exp(-\Delta E_G/RT) \int \sinh \sigma(t)/\sigma^* dt \quad (3)$$

where $G(t)$ is the craze length at time t . In a strain-bending apparatus, the deformation is held constant and the stress relaxes with time. For glassy polymers well below their glass transition temperatures, the relaxation times tend to be long relative to the time scale of a typical test, and a constant average value of the stress $\sigma(t) \approx (\sigma) = E_0\epsilon$, may be used in the integrand of Equation 3. Integration

of Equation 3 yields:

$$G(t) = G_0 \exp(-\Delta E_G/RT) \times [(\sinh E_0\epsilon/\sigma^*)]t = A'(\sinh B\epsilon)t \quad (4)$$

where

$$A' = G_0 \exp(-\Delta E_G/RT) \quad (5)$$

and

$$B = E_0/\sigma^* \quad (6)$$

The quantity A' has the dimensions of length per unit time, and may be interpreted as a characteristic growth-rate constant for a given polymer-crazing agent system. It depends exponentially on temperature, so that the activation energy for craze growth, ΔE_G , may be calculated from a plot of $\ln A'$ against T^{-1} .

The quantity $(1/B)$ has the dimensions of a strain (i.e. is dimensionless), and may be interpreted as a characteristic strain constant for a given polymer. It should be relatively independent of temperature, well below the glass transition temperature of the polymer.

3. Experimental procedure

Experiments were conducted on a variable radius of curvature strain-bending apparatus fashioned after that designed by Stolki and Haslett [6]. Rectangular test specimens 250 mm by 50 mm of Lexan polycarbonate were cut from 8 mm thick sheets and then annealed and dried at 100°C for 24 h under vacuum. The strain-bending apparatus is shown in Fig. 1. A test specimen was flexed over the surface of the apparatus and attached to the metal block with a pair of grips as shown. The strain ϵ , in the test specimen at any point is given by:

$$\epsilon = d/R \quad (7)$$

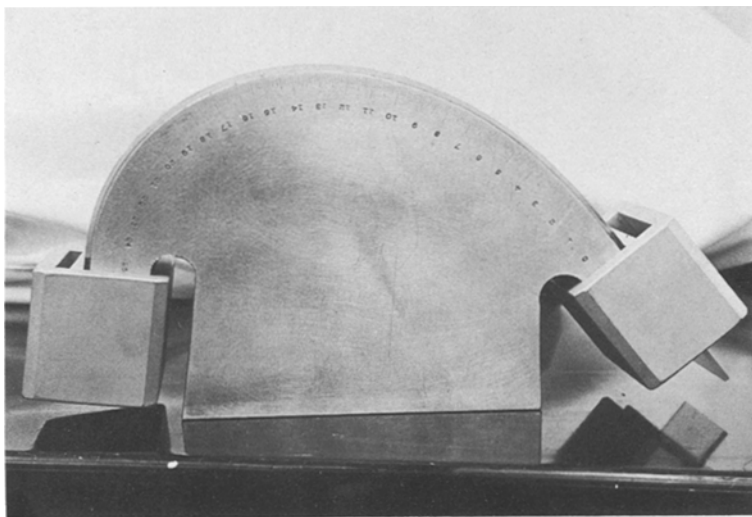


Figure 1 The strain-bending apparatus.

where d is the half-thickness of the specimen and R is the radius of curvature at the neutral axis of the flexed sample. In order to obtain the most accurate values of strain as a function of position along the surface, a calibration was carried out using HBM 3/120 LY58 strain gauges, glued at each point of measurement to a 0.35 mm thick strip of steel mounted in the same manner as a test specimen. A millimetric scale was etched on one edge of the apparatus adjacent to the mounting surface, and the strain was measured as a function of position along the surface. The strains thus obtained were identical to the calculated strains based on the dimensions and radius of curvature of the surface. The strains in the test specimen were thus calculated from the dimensions of the system.

The strain-bending apparatus, with test specimen mounted, is placed in an open glass vessel containing the solvent at the temperature of the test. A cover is placed over the top of the vessel to minimize evaporation losses. To maintain a constant temperature, the vessel containing the apparatus is placed in a thermostatically controlled water bath, also of glass, so that the water nearly reached the top of the immersed vessel. The test apparatus is positioned in such a manner that the

crazes forming on the surface of the test specimen can be seen and photographed. A typical photograph is shown in Fig. 2. In this study, the cut edges of the specimen were coated with an epoxy resin to isolate them from the solvent. Therefore, the crazes nucleated on the surface at the centre of the test piece. Nucleation occurs first at the point of highest strain, and then the craze-front moves up the surface. Both the rate of nucleation and the growth of crazes can be determined by measuring the length of an individual craze as a function of time, using a cathetometer. Craze growth will be described in this paper; nucleation rate will be described in a subsequent presentation.

4. Experimental results

The experiments were carried out on Lexan polycarbonate immersed in normal hexane, *n*-heptane, *n*-octane, *n*-decane and *n*-dodecane, at temperatures ranging from 293 to 333 K. Typical sets of experimental values for the rate of craze growth, dG/dt , as a function of strain, ϵ_T , are illustrated in Fig. 3 for polycarbonate in *n*-octane, and in Fig. 4 for polycarbonate in *n*-dodecane.

A master curve for the craze growth rate at a reference temperature may be calculated by using

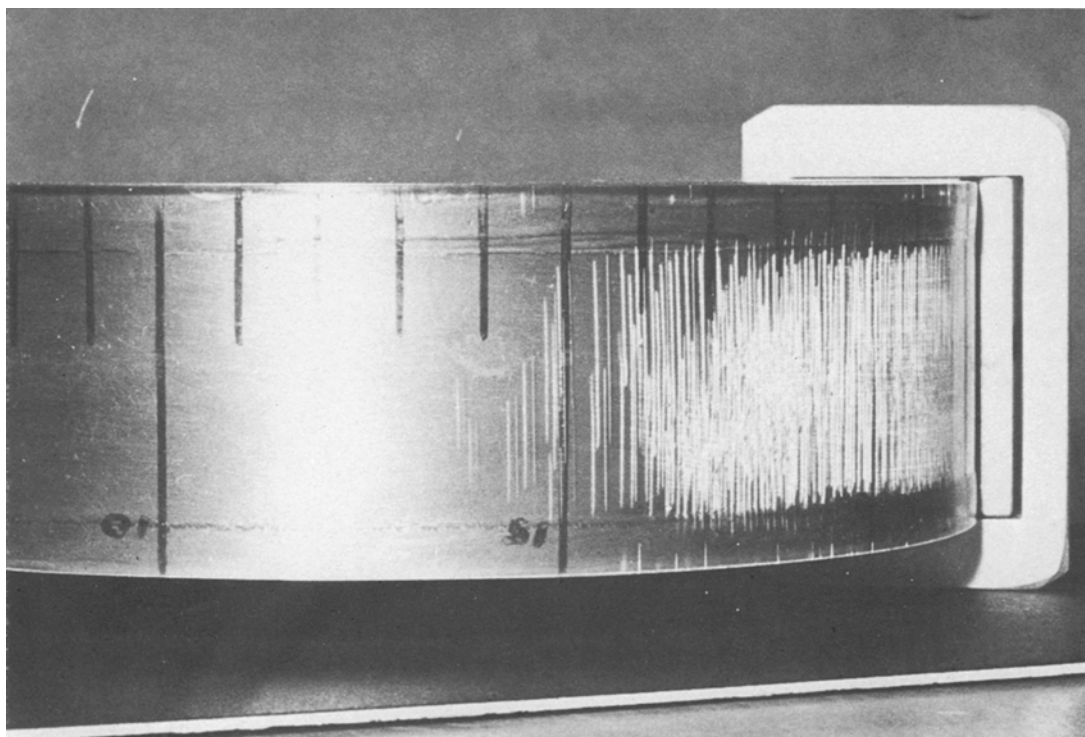


Figure 2 Crazes growing on a polycarbonate specimen exposed to a normal hydrocarbon.

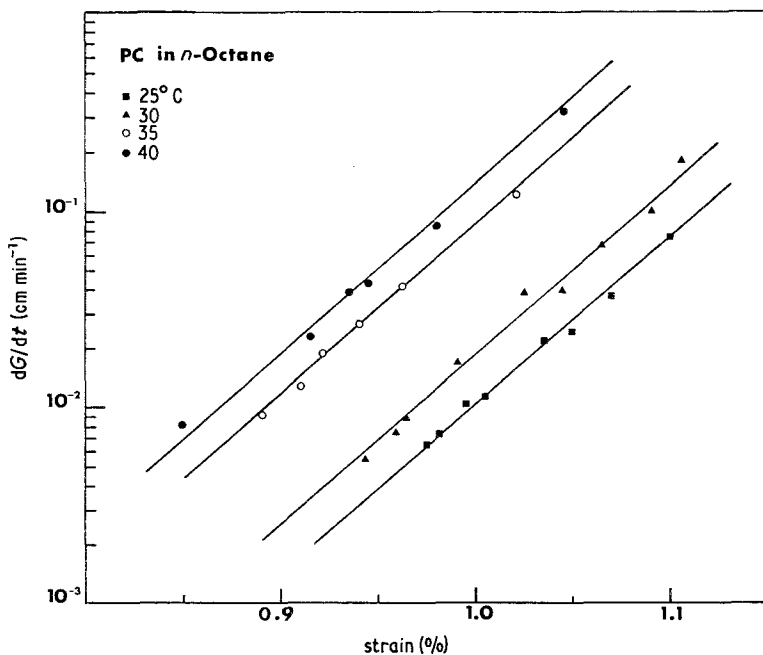


Figure 3 Craze growth as a function of per cent strain for polycarbonate in *n*-octane at various temperatures.

the principle of the equivalence of strain and temperature as they affect the growth rate. Equating two values of dG/dt at two temperatures T and T_R , one obtains:

$$\begin{aligned} (dG/dt)_T &= (dG/dt)_{T_R} \\ &\approx G_0 \exp(-\Delta E_G/RT + B\epsilon_T) \\ &= G_0 \exp(-\Delta E_G/RT_R + B\epsilon_{T_R}) \quad (8) \end{aligned}$$

Equation 8 may be rewritten as

$$\epsilon_T = \epsilon_{T_R} [(-\Delta E_G/RB)(T_R^{-1} - T^{-1})]. \quad (9)$$

Thus, $(dG/dt)_{T_R}$ may be plotted at any given reference temperature, T_R , as a function of the strain, ϵ_{T_R} . The master curve may be used at any other temperature, T , by recalculating the strain to the "equivalent" values, ϵ_T using Equation 8. The data shown in Fig. 3 at the four temperatures used were shifted in this manner to a reference temperature of $T = 303$ K, and the result is shown in

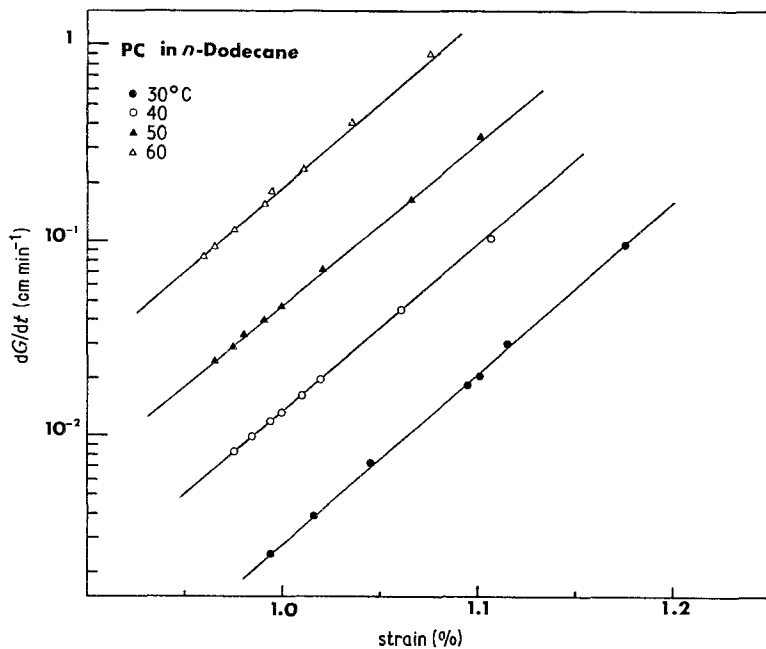


Figure 4 Craze growth as a function of per cent strain for polycarbonate in *n*-dodecane at various temperatures.

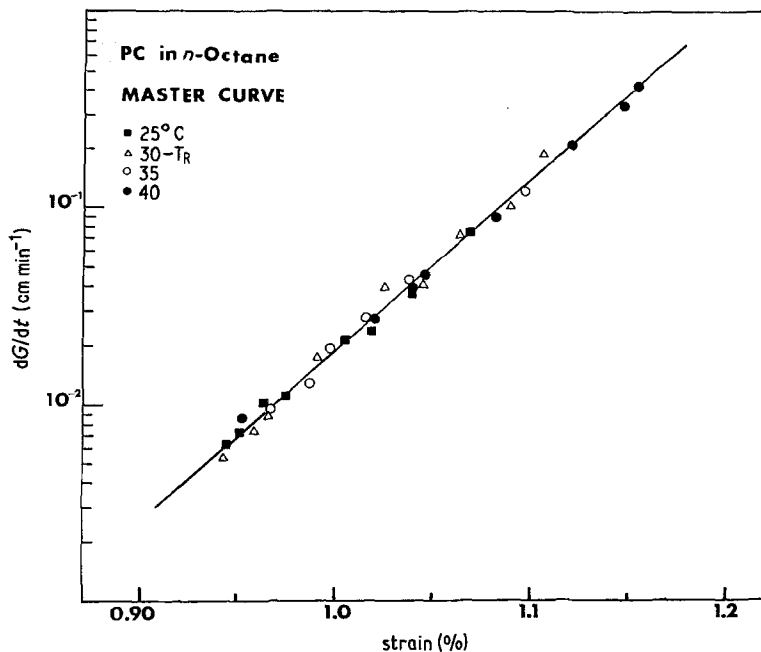


Figure 5 A master curve for craze growth as a function of per cent strain at a reference temperature of 303 K for polycarbonate in *n*-octane.

Fig. 5. The master curves at $T = 303$ K for three other polycarbonate/crazing agent combinations are shown in Fig. 6 (without data points to avoid confusion). For the range of variables studied, the maximum value of B was of the order of 1800, so the hyperbolic sine function is well approximated by an exponential, and Equation 4 may be differentiated and rewritten as

$$\ln(dG/dt) = \ln A'/2 + B\epsilon. \quad (10)$$

It can be seen from Figs. 3 to 6 that the $\ln dG/dt$ varies linearly with strain and that the slopes are the same for each crazing agent in the homologous series. Thus, the dimensionless parameter B is a constant, independent of both solvent and temperature. A linear regression analysis was used to evaluate A' and B at each of the temperatures used.

It was found that a constant value of $B = 2000 \pm 10\%$ provided the best fit of the experimental data.

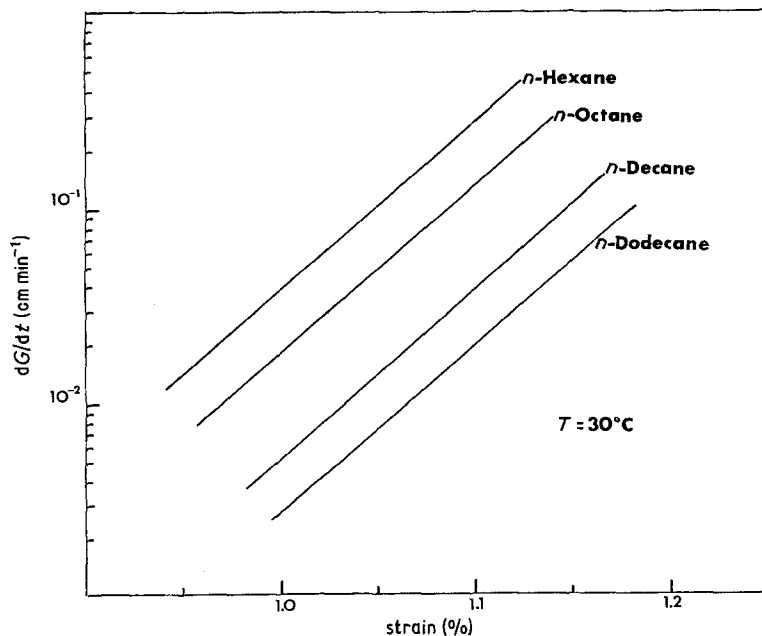


Figure 6 Master curves for craze growth as a function of per cent strain at a reference temperature of 303 K for polycarbonate in *n*-hexane, *n*-octane, *n*-decane and *n*-dodecane.

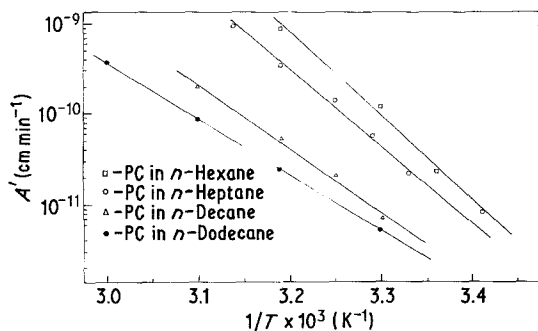


Figure 7 Semi-logarithmic plots of the craze growth rate parameter A' as a function of T^{-1} for polycarbonate in *n*-hexane, *n*-heptane, *n*-decane and *n*-dodecane.

The growth rate parameter A' was found to vary exponentially with temperature (Equation 5) and also depended upon the crazing agent used, as illustrated by Fig. 7. Using Equation 5, one may determine the rate constant G_0 and the activation energy ΔE_G from a linear regression analysis of the curves in Fig. 7. The values thus obtained are tabulated in Table I, along with the solubility parameters for the various materials. Both the $\ln G_0$ and ΔE_G are shown to be linear functions of the square of the difference between the solubility parameter of the polymer and the crazing agent, $(\delta_p - \delta_s)^2$ (Figs. 8 and 9, respectively).

Figs. 8 and 9 indicate a strong correlation between the craze growth rate and the thermodynamic properties of the polymer/crazing agent system, as has been often shown in the literature [7]. With this particular homologous series of normal hydrocarbons, the simplest criteria for compatibility are the Hildebrand solubility parameter δ , [8], and the Flory interaction parameter χ_s , [9], where

$$\chi_s \propto (\delta_p - \delta_s)^2. \quad (11)$$

If the rate process is diffusion controlled, as has been suggested [10,11], the rate constant A' should follow an Arrhenius-type relationship,

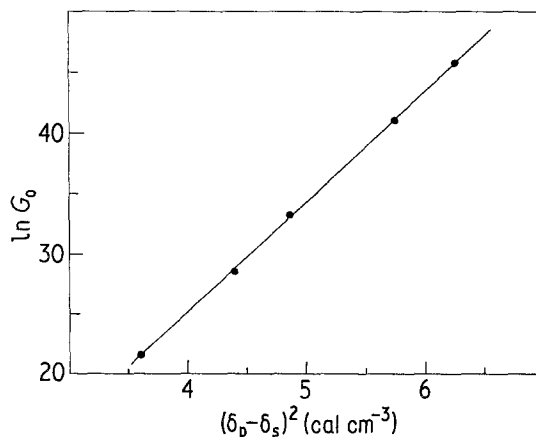


Figure 8 A linear plot of the pre-exponential constant $\ln G_0$ as a function of the square of the differences between the solubility parameters of the polymer and the crazing agent, $(\delta_p - \delta_s)^2$, for polycarbonate in normal hydrocarbons.

with a pre-exponential constant related to an entropy of activation, and an exponential factor related to an enthalpy of activation

$$A' \propto (\exp \Delta S_G/R)(\exp -\Delta H_G/RT) \quad (12)$$

Thus $\ln G_0$ is proportional to ΔS_G and ΔE_G is proportional to ΔH_G . As the polymer and crazing agent become more compatible and closer in size and shape, $(\delta_p - \delta_s)^2$ decreases, and both the entropic and enthalpic terms decrease.

The latter arguments are not meant to be quantitative; in general, polymer/crazing agent systems are too complex thermodynamically to be described well using ideal solution theories. Such arguments may be useful, however, in defining some correlating parameters for describing kinetic data.

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TABLE I Solubility parameters and kinetic parameters for polycarbonate and *n*-hydrocarbons

| Material | Solubility parameter, δ_s (cal cc ⁻¹) ^{1/2} | $(\delta_p - \delta_s)^2$ (cal cc ⁻¹) | Activation energy for craze growth ΔE_G (cal (g-mol) ⁻¹) | Rate constant for craze growth $\ln G_0$ (G_0 in cm min ⁻¹) |
|--------------------|--|--|--|--|
| Polycarbonate | ($\delta_p = 9.8$) | — | — | — |
| <i>n</i> -hexane | 7.3 | 6.25 | 41 360 | 45.58 |
| <i>n</i> -heptane | 7.4 | 5.76 | 38 920 | 40.83 |
| <i>n</i> -octane | 7.6 | 4.84 | 34 050 | 33.55 |
| <i>n</i> -decane | 7.7 | 4.41 | 32 200 | 27.91 |
| <i>n</i> -dodecane | 7.9 | 3.61 | 28 130 | 21.54 |

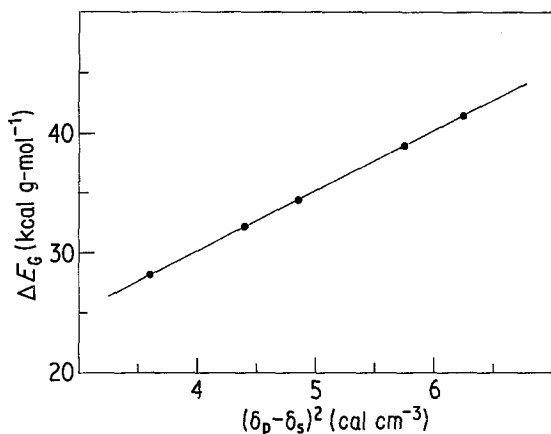


Figure 9 A linear plot of the activation energy for craze growth, E_G , as a function of the square of the differences between the solubility parameters of the polymer and the crazing agent, $(\delta_p - \delta_s)^2$, for polycarbonate in normal hydrocarbons.

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