

The Mechanism and Energy of Activation of the Melting of Poly(ϵ -caprolactone) with and Without Prior Treatment with Span 80

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ABSTRACT: Differential scanning calorimetry (DSC) is used to determine the energy of activation and melting mechanism of PCL and of mixtures of PCL with the surfactant Span 80. The melting of poly(ϵ -caprolactone) follows a nucleation and growth model with an Avrami exponent of 4. Addition of Span 80

reduces the energy of activation of this process. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3635–3640, 2011

Key words: DSC; activation energy; PCL; solid state mechanisms

INTRODUCTION

Poly(ϵ -caprolactone) (PCL; see Fig. 1) is a crystalline aliphatic polyester¹ with a melting point T_m of 68.3°C and a glass transition temperature T_g of –63°C. It is obtained via enzymatic cleavage of the ϵ -caprolactone ring (Fig. 2) by porcine pancreatic lipases.² The degree of polymerization achieved depends on the reaction conditions. PCL is very hydrophobic and in the absence of appropriate enzymes undergoes only very slow degradation both *in vitro* and *in vivo*. Its adoption of a lamellar structure in the solid state (Fig. 3) makes it suitable for sandwiching³ and coating⁴ and it is commonly used in this way for sustained release of drugs from pharmaceutical dosage forms.

Because PCL sandwiches and coatings are formed by incorporating the substance to be covered in molten PCL, it is desirable to lower the melting point of the latter, primarily to avoid damage to the substance to be covered. As with other crystalline polymers, this can be achieved by treating the molten polymer with surfactants that weaken the interactions among polymer chains and thus lower the melting point of the solidified mixture.^{5,6} To understand these processes, it is of interest to determine the energy of activation and mechanism of the melting of the pure and surfactant-treated polymer.

In the work described here, we used differential scanning calorimetry (DSC)⁷ to determine the energy of activation and melting mechanism of PCL and of mixtures of PCL with the surfactant Span 80 (sorbitan monooleate; Fig. 4).

Following the standard treatment of the kinetics of solid-state processes, we assume that the rate of melting of a substance is given by an equation of the form

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

where α is the proportion of the substance that has melted, t is the time, f is a function of α that is independent of the temperature T , and the temperature dependence of the rate constant k is given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad (2)$$

where E_a is the energy of activation, R the gas constant, and A the pre-exponential factor. If the temperature is varied at a constant rate β , eq. (1) can be rewritten in the form

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-\frac{E_a}{RT}} \quad (3)$$

formal integration of which from $T = 0\text{K}$ defines a function $g(\alpha)$:

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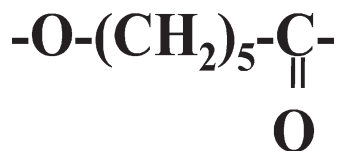


Figure 1 Molecular formula of poly(ϵ -caprolactone).

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-\frac{E_a}{RT}} dT \quad (4)$$

This integral function is either a sigmoidal function or a deceleration function. Table I shows different expressions of $g(\alpha)$. These functions were satisfactorily employed for the estimation of the reaction solid state mechanism.^{8–10} Models are classified by the underlying assumptions:

- Nucleation: Formation and growth of nuclei are considered to be rate-limiting. Nucleation rate is different from the growth rate and the model accounts for both.
- Geometrical contraction: The progress of the product layer from the surface to the inner crystal is considered to be rate-limiting. It is different for various crystal morphologies (cubic, cylindrical, spherical, ...)
- Diffusion: Diffusion of reactant or product is considered to be rate-limiting.
- Reaction order: The rate law is based on considerations for homogeneous kinetics

Assuming that for melting processes $f(\alpha) = 1-\alpha$, then according to the corresponding form of Kissinger's expression,¹¹

$$\ln\left(\frac{\beta}{T_f^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_f} \quad (5)$$

(where T_f is the temperature of the DSC melting peak), E_a can be determined by running scans at several different heating rates β and fitting straight lines to plots of β/T_f^2 against $1/T_f$.

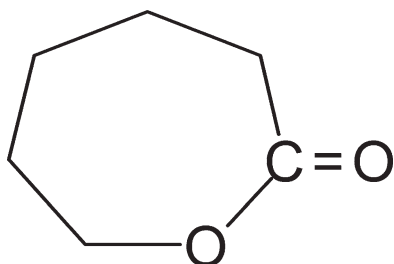


Figure 2 The ϵ -caprolactone ring.

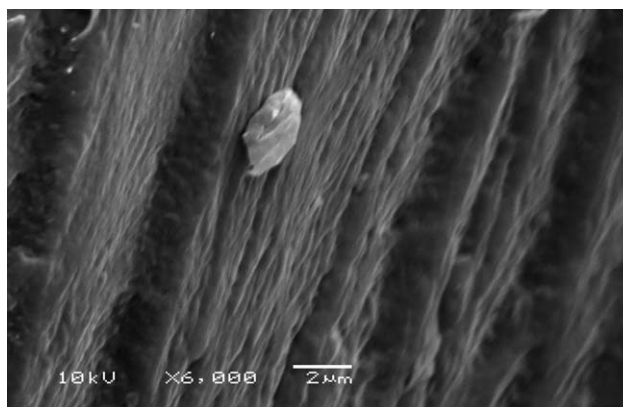


Figure 3 Solid-state lattice structure of poly(ϵ -caprolactone).

Alternately, integration of the right-hand side of eq. (4) using Doyle's approximation¹² affords

$$\log(\beta) = \log\left[\frac{AE_a}{g(\alpha)R}\right] - 2.315 - \frac{0.457E_a}{RT} \quad (6)$$

Following Ozawa¹³ and Flynn and Wall,¹⁴ this expression allows estimation of E_a by first running scans at several different heating rates β , then determining in each case, by numerical integration of the scan peak, the temperatures at which α reaches a given series of values, and finally plotting $\log \beta$ against $1/T$ for each of these values of α (because of the approximation involved in eq. (6), α should be no greater than 20%).

If the mechanism of melting and the corresponding functional form of $g(\alpha)$ are known, a third means of determining E_a is to use Coats and Redfern's¹⁵ asymptotic solution of eq. (4),

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (7)$$

which after numerical integration of a scan peak to determine the temperatures at which α reaches a given series of values, allows E_a to be estimated from a plot of $\ln(g(\alpha)/T^2)$ against $1/T$. Moreover, if the mechanism of melting is not known, it may be inferred, and E_a estimated simultaneously, by applying this procedure to the functions $g(\alpha)$

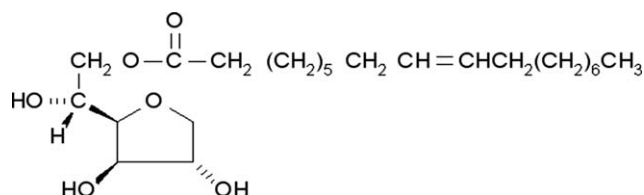


Figure 4 Molecular formula of sorbitan monooleate (Span 80).

TABLE I
Melting Mechanisms Considered in this Study, with the Corresponding Functions $g(\alpha)$

Symbol	$g(\alpha)$	Mechanism
A_2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth [Avrami eq. (1)]
A_3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth [Avrami eq. (2)]
A_4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth [Avrami eq. (3)]
R_1	α	One-dimensional motion
F_1	$[-\ln(1-\alpha)]$	Random nucleation
D_1	α^2	One-dimensional diffusion

corresponding to a series of possible mechanisms, and finding that which affords the lowest E_a .

The Kissinger and Flynn-Wall-Ozawa methods have the advantage that they do not require previous knowledge of the reaction mechanism for determining the activation energy. The following authors use the thermodegradation energies obtained using these methods to check mechanism models.⁸⁻¹⁰

EXPERIMENTAL

Materials and sample preparation

Poly(ϵ -caprolactone) (PCL) was supplied by Aldrich in the form of pellets 5-mm long and 2 mm in diam-

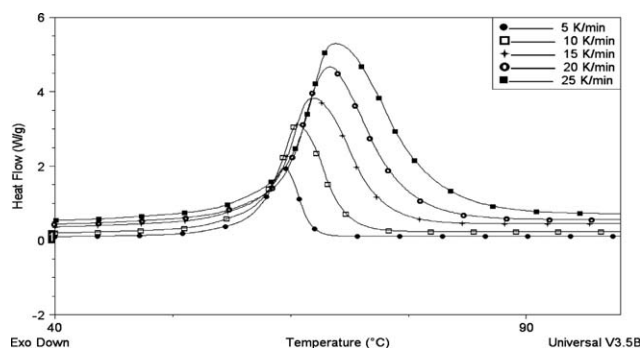


Figure 5 A typical DSC thermograms of poly(ϵ -caprolactone) mixture of poly(ϵ -caprolactone) and Span 80 recorded at the indicated heating rates.

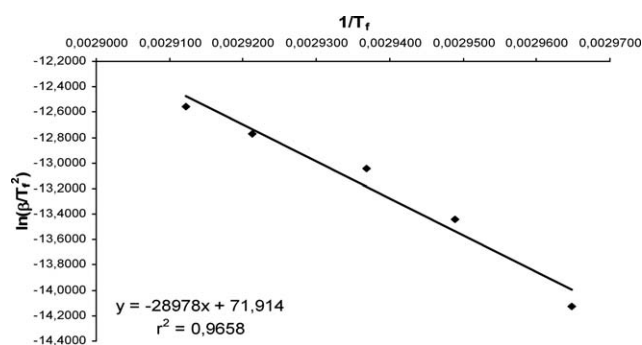


Figure 6 A typical Kissinger plot for the melting of poly(ϵ -caprolactone) mixture of poly(ϵ -caprolactone) and Span 80.

TABLE II
Energies of Activation E_a of Poly(ϵ -caprolactone) and Poly(ϵ -caprolactone)/Span 80 Mixtures with Span 80 Contents of 5, 10, and 20%, as Estimated by Kissinger's Method, Together with Their Standard Deviations and the Coefficients of Determination of the Corresponding Regression Lines

	E_a (kJ/mol)	r^2
PCL	241 ± 26	0.9658
5% SPAN [®] 80	241 ± 30	0.9702
10% SPAN [®] 80	261 ± 29	0.9648
20% SPAN [®] 80	249 ± 29	0.9635

eter (Ref. 181609, polycaprolactone), and Span 80 by Fluka (Ref. 85548). Appropriate quantities of pellets were ground, melted, and mixed with Span 80 (when required) to obtain mixtures with Span 80 contents of 0, 5, 10, and 20%.

DSC

Samples were heated from 15 to 250°C under a stream of dry nitrogen (flow rate 50 mL/min) in a TA Instruments computer-controlled Q100 DSC calorimeter, at heating rates of 5, 10, 15, 20, and 25°C/min. All experiments were performed in triplicate, and the T_f and (α, T) values used in subsequent analyses were the means of the three determinations.

RESULTS AND DISCUSSION

Kissinger's method has been used to determine the activation energy of solid-state reactions without a precise knowledge of the reaction mechanism. Figure 5 shows a set of DSC thermograms typical of

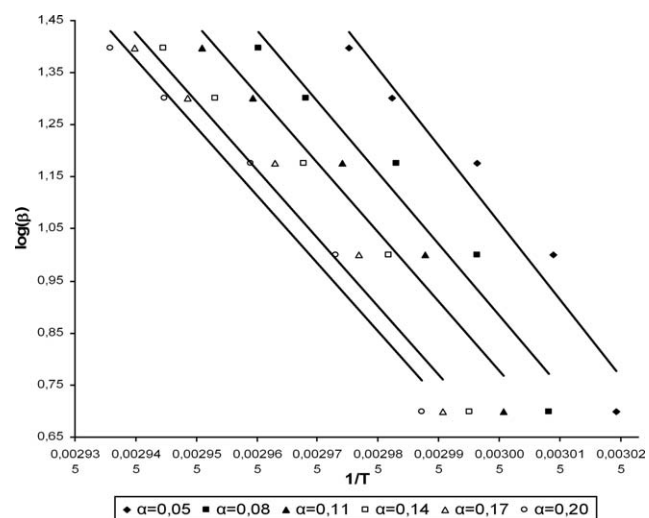


Figure 7 A typical Flynn-Wall-Ozawa plots of poly(ϵ -caprolactone) mixture of poly(ϵ -caprolactone) and Span 80.

TABLE III
Energies of Activation E_a of Poly(ϵ -caprolactone) and Poly(ϵ -caprolactone)/Span 80 Mixtures with Span 80 Contents of 5, 10, and 20%, as Estimated by the Flynn-Wall-Ozawa Method at Several Values of the Extent of Melting α , Together with Their Standard Deviations and the Coefficients of Determination of the Corresponding Regression Lines

α	PCL		5% SPAN [®] 80		10% SPAN [®] 80		20% SPAN [®] 80	
	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2
0.05	255 ± 31	0.9567	214 ± 34	0.9306	216 ± 33	0.9332	234 ± 32	0.9480
0.08	237 ± 27	0.9624	206 ± 30	0.9394	210 ± 30	0.9437	223 ± 27	0.9575
0.11	231 ± 25	0.9668	201 ± 28	0.9449	207 ± 27	0.9502	215 ± 25	0.9619
0.14	229 ± 23	0.9706	198 ± 27	0.9490	203 ± 26	0.9539	210 ± 23	0.9653
0.17	229 ± 22	0.9735	197 ± 25	0.9533	200 ± 25	0.9569	205 ± 22	0.9682
0.20	229 ± 21	0.9754	198 ± 24	0.9570	198 ± 23	0.9607	204 ± 20	0.9718

TABLE IV
Energies of Activation E_a of Poly(ϵ -caprolactone) and Poly(ϵ -caprolactone)/Span 80 Mixtures with Span 80 Contents of 5, 10, and 20%, as Estimated by the Coats-Redfern Method for Several Melting Models (see Table I) at Several Heating Rates β , Together with Their Standard Deviations and the Coefficients of Determination of the Corresponding Regression lines

b (°C/min)	PCL		5% SPAN [®] 80		10% SPAN [®] 80		20% SPAN [®] 80	
	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2	E_a (kJ/mol)	r^2
(a) Mechanism A_2								
5	181.2 ± 1.0	0.9994	127.0 ± 0.3	0.9999	126.7 ± 0.1	0.99998	140.1 ± 0.2	0.99995
10	163.3 ± 1.4	0.9987	114.2 ± 0.3	0.9998	113.5 ± 0.2	0.99996	124.3 ± 0.5	0.99969
15	156.2 ± 1.5	0.9983	113.5 ± 0.4	0.9998	110.5 ± 0.2	0.99996	118.1 ± 0.2	0.99997
20	154.3 ± 2.2	0.9961	111.4 ± 0.6	0.9995	115.8 ± 0.5	0.99969	116.8 ± 0.2	0.99995
25	152.7 ± 2.5	0.9949	112.6 ± 0.9	0.9986	106.6 ± 0.3	0.99984	112.9 ± 0.4	0.99974
(b) Mechanism A_3								
5	118.9 ± 0.7	0.9994	82.8 ± 0.2	0.9999	82.7 ± 0.1	0.99998	91.6 ± 0.2	0.99995
10	107.0 ± 0.9	0.9986	74.4 ± 0.2	0.9998	73.9 ± 0.1	0.99996	81.0 ± 0.3	0.99968
15	102.2 ± 1.0	0.9982	73.8 ± 0.3	0.9998	71.9 ± 0.1	0.99996	76.9 ± 0.1	0.99997
20	101.0 ± 1.5	0.9960	72.4 ± 0.4	0.9995	75.4 ± 0.3	0.99967	76.0 ± 0.1	0.99995
25	99.9 ± 1.7	0.9947	73.2 ± 0.7	0.9985	69.2 ± 0.2	0.99983	73.5 ± 0.3	0.99972
(c) Mechanism A_4								
5	87.9 ± 0.5	0.9994	60.8 ± 0.1	0.9999	60.7 ± 0.1	0.99998	67.4 ± 0.1	0.99995
10	78.9 ± 0.7	0.9986	54.4 ± 0.2	0.9998	54.1 ± 0.1	0.99996	59.4 ± 0.3	0.99967
15	75.3 ± 0.7	0.9982	54.0 ± 0.2	0.9998	52.5 ± 0.1	0.99996	56.3 ± 0.1	0.99997
20	74.3 ± 1.1	0.9959	53.0 ± 0.3	0.9995	55.2 ± 0.24	0.99966	55.7 ± 0.1	0.99995
25	73.5 ± 1.3	0.9945	53.6 ± 0.5	0.9984	50.5 ± 0.2	0.99982	53.7 ± 0.2	0.99971
(d) Mechanism R_1								
5	346.4 ± 1.0	0.9998	243.9 ± 0.3	0.99997	243.4 ± 0.8	0.9998	268.7 ± 0.4	0.99996
10	312.8 ± 1.7	0.9994	220.0 ± 0.2	0.99998	218.6 ± 0.9	0.9997	238.9 ± 0.4	0.99995
15	299.3 ± 2.0	0.9992	218.6 ± 0.2	0.99998	212.9 ± 0.9	0.9997	227.3 ± 0.4	0.99993
20	295.8 ± 3.3	0.9976	214.7 ± 0.5	0.99989	223.0 ± 1.5	0.9992	224.8 ± 0.4	0.99994
25	292.9 ± 3.9	0.9966	217.1 ± 1.3	0.99936	205.6 ± 1.0	0.9995	217.6 ± 0.7	0.99982
(e) Mechanism F_1								
5	368.0 ± 2.0	0.9994	259.3 ± 0.6	0.9999	258.7 ± 0.2	0.99998	285.6 ± 0.5	0.99995
10	332.2 ± 2.8	0.9987	233.9 ± 0.7	0.9998	232.5 ± 0.3	0.99996	253.9 ± 1.0	0.99970
15	317.9 ± 3.0	0.9983	232.4 ± 0.8	0.9998	226.4 ± 0.3	0.99996	241.6 ± 0.3	0.99997
20	314.2 ± 4.4	0.9963	228.2 ± 1.1	0.9995	237.1 ± 0.9	0.99971	239.0 ± 0.4	0.99995
25	311.0 ± 5.0	0.9951	230.7 ± 1.9	0.9986	218.6 ± 0.6	0.99985	231.4 ± 0.8	0.99975
(f) Mechanism D_1								
5	698.4 ± 2.0	0.9998	493.3 ± 0.6	0.99997	492.2 ± 1.7	0.99978	542.8 ± 0.8	0.99996
10	631.1 ± 3.5	0.9994	445.5 ± 0.5	0.99998	442.7 ± 1.7	0.99972	483.1 ± 0.7	0.99996
15	604.1 ± 3.9	0.9992	442.7 ± 0.4	0.99998	431.3 ± 1.7	0.99970	460.0 ± 0.9	0.99993
20	597.3 ± 6.7	0.9976	434.9 ± 1.0	0.99990	451.4 ± 2.9	0.99921	455.1 ± 0.8	0.99994
25	591.3 ± 7.9	0.9967	439.7 ± 2.5	0.99938	416.6 ± 2.0	0.99954	440.8 ± 1.3	0.99982

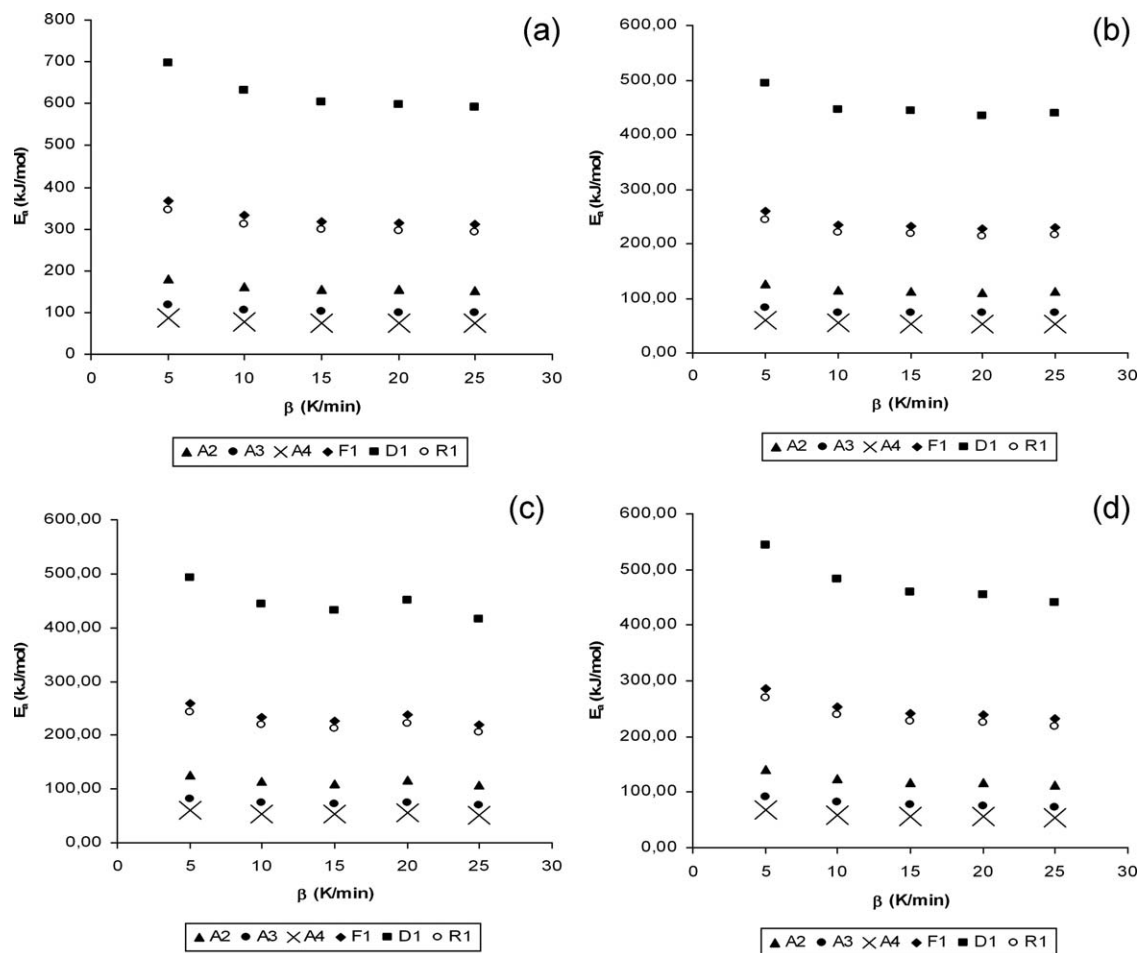


Figure 8 Values of E_a estimated by the Coats-Redfern method, using the indicated heating rates β and assuming various melting mechanisms (see Table I), for the melting of poly(ϵ -caprolactone) (a) and poly(ϵ -caprolactone)/Span 80 mixtures with Span 80 contents of 5 (b), 10, (c) and 20% (d).

those recorded in these experiments. Application of Kissinger's method (Fig. 6 shows an example) afforded E_a values of 241–261 kJ/mol (Table II), but

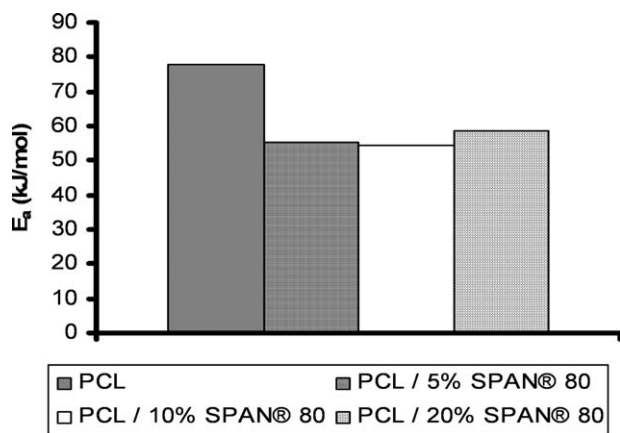


Figure 9 Values of E_a , estimated by the Coats-Redfern method assuming the melting mechanism A_4 (see Table I), for the melting of poly(ϵ -caprolactone) and poly(ϵ -caprolactone)/Span 80 mixtures with Span 80 contents of 5, 10, and 20%.

the limited linearity of the fits ($r^2 = 0.9635$ – 0.9702) meant that the precision of these estimates (26–30 kJ/mol) was insufficient to distinguish among the four formulations assayed. Likewise, although the parallelism among the lines fitted in application of the Flynn-Wall-Ozawa method corroborated its applicability to the system studied (Fig. 7), and the E_a estimates for 5 and 10% mixtures were lower, for

TABLE V
Energies of Activation E_a Estimated by the Coats-Redfern Method Assuming the Melting Mechanism A_4 (see Table I), for the Melting of Poly(ϵ -caprolactone) and Poly(ϵ -caprolactone)/Span 80 Mixtures with Span 80 Contents of 5, 10, and 20%; Means of Values Estimated from DSC Thermograms Obtained at Heating Rates of 5, 10, 15, 20, and 25 °C/min

	E_a (kJ/mol)
PCL	78.0 ± 0.3
PCL / 5% SPAN [®] 80	55.1 ± 0.2
PCL / 10% SPAN [®] 80	54.6 ± 3.8
PCL / 20% SPAN [®] 80	58.5 ± 5.4

given α , than those of the 0 and 20% mixtures (198–216 as against 204–255 kJ/mol; Table III), precision was again insufficient (20–34 kJ/mol overall, 23–34 kJ/mol for the 5 and 10% mixtures).

The Coats-Redfern approach afforded much more precise estimates (0.06–7.90 kJ/mol overall; Table IV), especially for the 5 and 10% mixtures (0.06–2.90 kJ/mol). Whatever the Span 80 content and heating rate, the $g(\alpha)$ functions of the various melting mechanisms afforded E_a values that ranked the mechanisms in the order $A4 < A3 < A2 < R1 < F1 < D1$ (Fig. 8; see Table I for the nomenclature). $A4$, the nucleation and growth mechanism corresponding to Avrami's eq. (3), was accordingly identified as the melting mechanism of these systems. Averaging E_a over heating rates for this mechanism confirms that addition of Span 80 significantly lowers activation energy (i.e. Span80 is an efficient plasticizer for PCL), and that E_a is probably lowest with a Span 80 content of around 5–10% (Fig. 9 and Table V).

CONCLUSIONS

The melting of poly(ϵ -caprolactone) follows a nucleation and growth model with an Avrami exponent of 4 ($g(\alpha) = [\ln(1/(1-\alpha))]^{1/4}$). Addition of Span 80 reduces the energy of activation of this process, the optimal

Span 80 content of the mixture probably being around 5–10%.

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