

Effect of Chemical Structure on Crystallization Behavior of Poly(phenylene alkylene dicarboxylate) (PPAD)

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Received 31 October 1996; accepted 26 April 1997

ABSTRACT: Various poly(*p*-phenylene alkylene dicarboxylates) (PPADs) were synthesized and their crystallization behavior was examined as functions of the length and the odd/even numbers of carbon atoms in the aliphatic component. PPADs with longer aliphatic units of even-numbered carbon atoms were found to crystallize faster than do those of other cases. The results are compared with the crystallization behavior of conventional poly(alkylene terephthalate)s (PATs), e.g., poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), which have the same chemical composition as the corresponding PPAD but the reversed direction of the ester group. The effects of this structural difference on the melting temperature and the crystallization kinetics are also discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1575–1582, 1997

Key words: poly(*p*-phenylene dicarboxylates); poly(alkylene terephthalates); melting temperature; isothermal crystallization; odd–even effect

INTRODUCTION

Poly(alkylene terephthalate)s (PATs), e.g., poly(ethylene terephthalate) (PET)^{1–8} and poly(butylene terephthalate) (PBT),^{9–11} have been used for fibers, bottles, and plastics due to their good chemical and physical properties. Most PATs are crystalline polymers. Thus, for the last two decades, numerous research efforts have been devoted to the study of the crystallization behavior of these materials in relation to their physical properties.

Recently, it was reported that the stability and nature of the mesophase are greatly influenced by the bond direction of the ester group in azoxybenzene polyesters¹² and thermotropic liquid crystal-

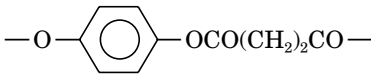
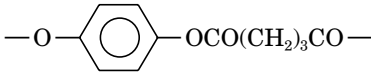
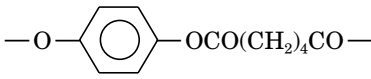
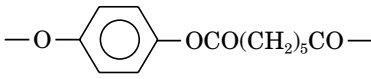
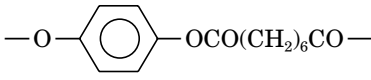
line polyesters with flexible aliphatic spacers.^{13–15} These phenomena have initiated explorative studies on the synthesis of poly(*p*-phenylene alkylene dicarboxylates) (PPADs) and their properties. PPADs contrast with PATs in a sense that the bond direction of the ester group in the repeat unit of PPADs is reversed as compared with the ester group in the repeat unit of PATs, i.e., PPADs have the repeat unit of the P—O—CO—A type, whereas PATs have the repeat unit of the P—CO—O—A type, where P and A represent the phenylene group and the alkylene group, respectively. This structural difference may result in different physical properties.

In this report, we synthesized several PPADs with different lengths of the aliphatic unit and examined their crystallization behavior. The behavior was systematically analyzed in terms of the length of the alkylene group and the odd/even numbers of carbon atoms in the alkylene unit. The thermal properties of PPADs are also com-

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Journal of Applied Polymer Science, Vol. 66, 1575–1582 (1997)
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Table I Polymerization Temperatures and Intrinsic Viscosities (IV) of the Various PPADs

Polymer	Repeat Unit	Sample Code	IV (dL/g)	Polymerization Temperature (°C)
Poly(phylene succinate)		PP2	0.33	120
Poly(phylene glutarate)		PP3	0.33	140
Poly(phylene adipate)		PP4	0.37	140
Poly(phylene pimelate)		PP5	0.30	140
Poly(phylene suberate)		PP6	0.41	140

pared with those of PATs and discussed in terms of the configurational effect of the ester group.

EXPERIMENTAL

Materials

Various PPADs of high molecular weight are synthesized by reacting equimolar parts of hydroquinone and appropriate aliphatic dicarboxylic acid chloride for 2 h at 120 or 140°C in an inert solvent, 1,1,2,2-tetrachloroethane (TCE). To obtain sufficiently high molecular weight polymers, the monomers are thoroughly purified: Hydroquinone is purified by recrystallization twice from acetone, and aliphatic dicarboxylic acid chloride is fractionally distilled under reduced pressure in an oil bath kept at 140°C or at 120°C. During polymerization, PPAD precipitates from the solution. The precipitate as a white solid polymer is filtered off, washed repeatedly with acetone, and then dried under a vacuum at 80°C for 3 days. The polymerization conditions of PPADs and their intrinsic viscosities measured in phenol (Ph)/TCE (6/4 w/w) at 25°C are listed in Table I.

For comparison, PET and PBT, supplied by Sunkyung Industry Co. (Korea), were also examined. The intrinsic viscosities of PET and PBT

measured in Ph/TCE (6/4 w/w) are 0.56 and 0.79, respectively.

Measurements

The configurational difference of the ester group between PATs and PPADs were examined by a Fourier transform infrared spectrometer (Model MIDAC FTIR). The samples were in a form of a KBr pellet. The thermal stability of PATs and PPADs was measured by a Perkin-Elmer TGA-7 under a N₂ atmosphere at the heating rate of 10°C/min. A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to study the crystallization behavior. Isothermal crystallization was observed by keeping the molten samples at 20°C above their melting temperatures for 3 min in order to destroy residual crystallites and then by rapidly cooling at the rate of 200°C/min to the predetermined isothermal crystallization temperature (T_c). The exotherm due to crystallization was recorded as a function of time.

RESULTS AND DISCUSSION

Figure 1 clearly shows the structural difference between PET and PP2 due to the ester group direction. It is well known that the C=O stretching

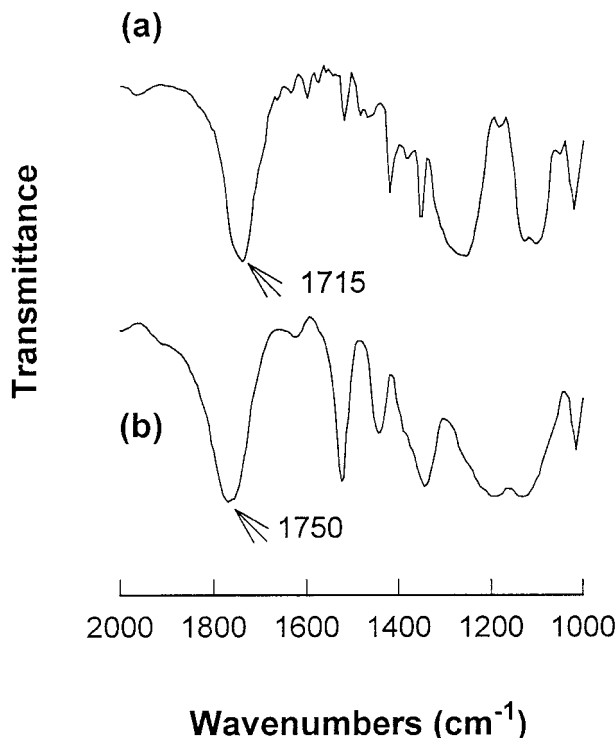


Figure 1 IR spectra of (a) PET and (b) poly(phenylene succinate) (PP2).

vibration in a normal ester group shifts to lower frequencies from the normal position (1735 cm^{-1}) when the carbonyl group is conjugated with the aryl group. On the contrary, it shifts to higher frequencies if the carbonyl group is activated by a single-bonded oxygen.¹⁶ As shown in Figure 1, the former effect is reflected on the C=O stretching vibration of PET (1715 cm^{-1}), and the latter effect, on that of PP2 (1750 cm^{-1}).

The melting temperatures and the heats of fusion of various PPADs are listed in Table II. It is clear from Table II that the melting temperature of PPADs decreases with increase in the length of the aliphatic unit. An odd–even effect on the melting temperature of PPADs is also observed: PPADs with even number of carbon atoms in aliphatic units exhibit larger heats of fusion than those PPADs with an odd number of carbon atoms. The melting temperature may be related to the crystallization rate and the heat of fusion (ΔH_f) of each polymer. Generally, polymers of higher melting temperature have a larger heat of fusion and fast crystallization.

PPADs have been reported to show higher melting temperatures when compared with PATs of an equal length of the aliphatic unit.^{17,18} This

may be ascribed to the increased intermolecular forces which come from enhanced chain rigidity, giving some hindrance to the rotation of the —OCO— group around the $\text{C}_6\text{H}_4\text{—O}$ axis in PPADs.

Isothermal crystallization was analyzed by employing the Avrami expression¹⁹

$$1 - X(t) = \exp(-kt^n) \quad (1)$$

where $X(t)$ is the weight fraction of the crystalline material at time t , calculated from the following equation:

$$X(t) = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt} \quad (2)$$

where dH/dt is the rate of heat evolution, k , the kinetic rate constant, and n , the Avrami exponent. Values of n can be obtained from the slope of the double-logarithmic plot, $\log[-\ln(1 - X(t))]$ versus $\log t$. Figures 2 and 3 show, respectively, the Avrami plots of PP2 and PP3. The kinetic parameters determined from the slopes and the intercepts of Figures 2 and 3 are listed in Table III. The n values for almost all PPADs except for PP5 lie between 3 and 4, which suggests the spherulitic crystal growth. It is, however, immature at this stage to draw a conclusion for the growth geometry and the type of nucleation from the exponent n value only, because of experimental uncertainties in determining n values from DSC and some ambiguity of the Avrami equation. The crystallization half-time ($t_{1/2}$) defined as the time taken for half of the crystallinity to develop is used for comparing the crystallization rate. The

Table II Melting Temperatures and Heats of Fusion of Various PPADs

Polymer	T_m (°C)	ΔH_f (J/g)
PP2	310	66.0
PP3	214	51.2
PP4	232	69.1
PP5	167	54.4
PP6	195	60.5

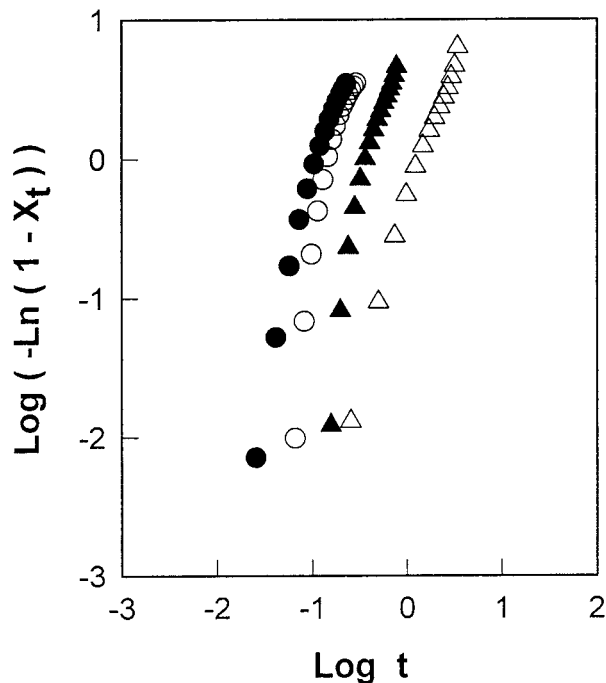


Figure 2 Avrami plots of poly(phenylene succinate) at various isothermal crystallization temperatures: (●) 275°C; (○) 282°C; (▲) 290°C; (△) 295°C.

value of $t_{1/2}$ is easily obtained from the following relation:

$$t_{1/2} = (\ln 2/k)^{1/n} \quad (3)$$

The crystallization half-times of PP2 and PET and of PP4 and PBT are plotted as a function of the degree of supercooling ΔT in Figures 4 and 5, respectively. The degree of supercooling, ΔT , defined as the difference between melting temperature and crystallization temperature, represents a driving force for crystallization.

It is well known that the crystallization rate depends on the crystallization temperature, the molecular weight of polymer, and the presence of a catalyst used for polymerization. Vilanova et al.⁸ reported that PET with a number-average molecular weight (\bar{M}_n) of about 9000 g/mol shows the maximum crystallization rate. Although there is some difference in the molecular weight of the two compared polymers, it is obvious that the crystallization rates of PP2 and PP4 are much faster than are those of PET and PBT, respectively. From the above result and the study of Gilbert and Hybart,¹¹ it may be concluded that PPADs crystallize more readily than do PATs.

Figure 6 shows the crystallization half-times of various PPADs as a function of ΔT . Two groups are categorized according to the crystallization behavior, i.e., each group has a similar crystallization half-time at a given ΔT . PPADs with even number of carbon atoms show lower crystallization half-times than do PPADs with an odd number of carbon atoms at the same ΔT . For numerical analysis, the crystallization rate expressed as $1/t_{1/2}$ was correlated with temperature by the general equation²⁰

$$\ln(1/t_{1/2}) = A_0 - K_2(T_m^0/T_c\Delta T) \quad (4)$$

$$\ln(1/t_{1/2}) = B_0 - K_3\{(T_m^0)^2/T_c(\Delta T)^2\} \quad (5)$$

where T_m^0 is the equilibrium melting temperature, and K_2 and K_3 are parameters representing the difficulty in the nucleation of the new phase for a two-dimensional nucleation mechanism and a three-dimensional nucleation mechanism, respectively, and depend on the interfacial free energy and the heat of fusion.^{21,22} In eqs. (4) and (5), the constants A_0 and B_0 depend on the density of nucleation and on the energy of transport of the molecules. The equilibrium melting temperature

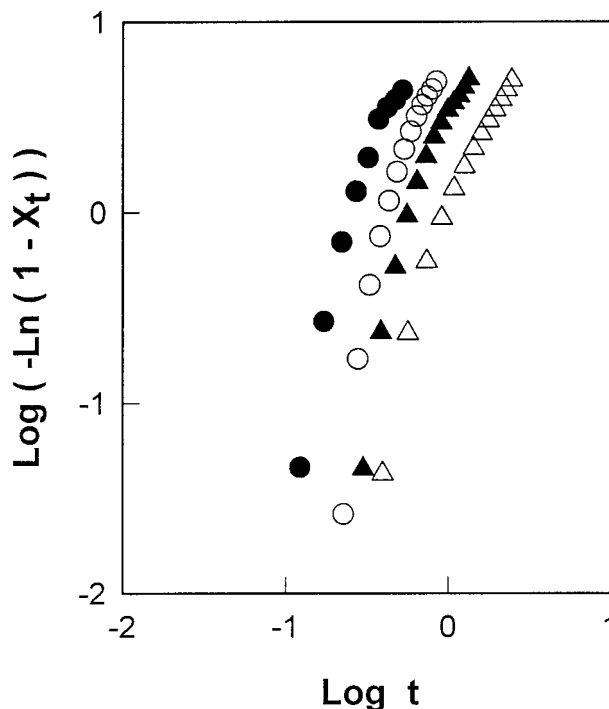


Figure 3 Avrami plots of poly(phenylene glutarate) at various isothermal crystallization temperatures: (●) 196°C; (○) 208°C; (▲) 212°C; (△) 216°C.

Table III Isothermal Crystallization Data of PET, PBT, and Various PPADs

Polymer	T_c (°C)	n^a	k^a	$t_{1/2}$ (min)
PET	195	3.0	0.74	0.98
	200	3.0	0.67	1.01
	205	2.0	0.64	1.04
	210	2.1	0.33	1.42
	215	3.0	0.04	2.58
	220	2.4	0.06	2.83
	225	2.5	0.02	4.52
PBT	160	2.5	14.45	0.29
	165	5.8	128.82	0.41
	170	4.9	28.25	0.47
	175	4.3	6.06	0.61
	178	3.7	2.05	0.75
	180	3.2	1.17	0.85
	182	3.2	0.70	1.00
PP2	275	2.7	279.1	0.17
	278	3.0	373.6	0.12
	282	3.5	498.2	0.15
	286	3.9	279.7	0.22
	290	3.2	15.1	0.38
	295	2.2	0.4	1.25
PP3	166	2.4	0.8	0.94
	170	3.2	65.8	0.24
	174	3.1	33.4	0.29
	178	3.5	14.5	0.42
	182	2.8	3.4	0.58
PP4	186	2.4	0.8	0.94
	210	2.8	9.6	0.39
	212	3.3	16.9	0.38
	214	3.5	3.2	0.65
	216	2.9	2.1	0.68
	218	2.7	0.5	1.13
PP5	220	2.6	0.1	2.24
	129	7.0	184.9	0.45
	131	7.0	133.9	0.47
	133	7.4	123.6	0.50
	135	6.3	30.0	0.55
	139	5.5	4.8	0.70
PP6	143	1.7	0.3	1.81
	175	2.6	0.7	1.01
	177	3.0	10.8	0.40
	181	3.1	5.9	0.50
	183	2.6	0.7	1.01

^a Average values with the standard deviation of 5%.

was determined by the relationship between the apparent melting temperature and the crystallization temperature (see Fig. 7). The numerical values of the equilibrium melting temperatures are 308°C for PP2, 214°C for PP3, 232°C for PP4, 167°C for PP5, and 195°C for PP6. When $\ln(1/t_{1/2})$ is plotted against $T_m^0/(T_c\Delta T)$ and $(T_m^0)^2/T_c$

$(\Delta T)^2$ as shown in Figures 8 and 9, respectively, straight lines are obtained. The values of K_2 and K_3 are obtained from the slopes of the plots and are listed in Table IV. It is interesting to note that the values of K_2 and K_3 are closely related to the crystallization rate. It is well known that the polymers containing longer aliphatic units, which lead

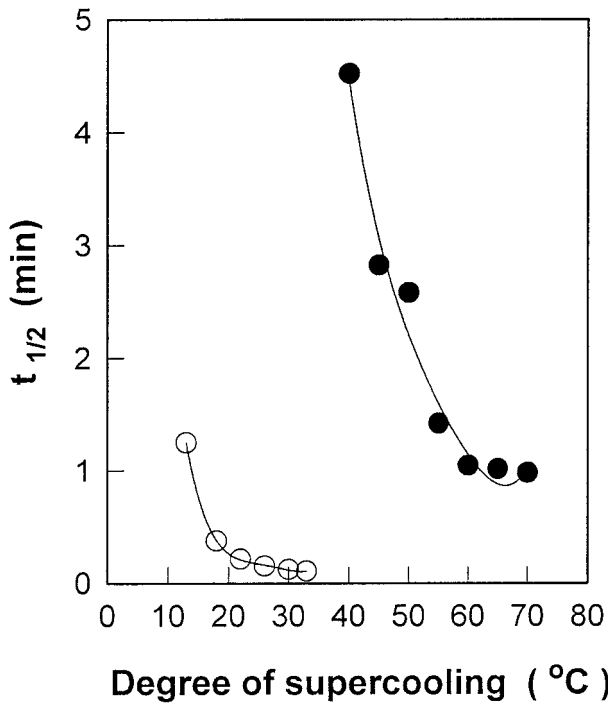


Figure 4 Comparison of crystallization half-time ($t_{1/2}$) between (●) PET and (○) poly(phenylene succinate) as a function of the degree of supercooling (ΔT).

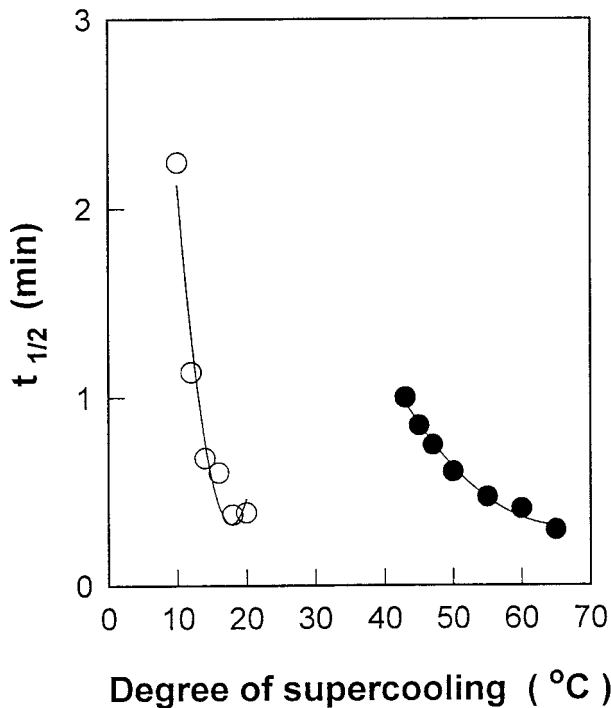


Figure 5 Comparison of crystallization half-time ($t_{1/2}$) between (●) PBT and (○) poly(phenylene adipate) as a function of the degree of supercooling (ΔT).

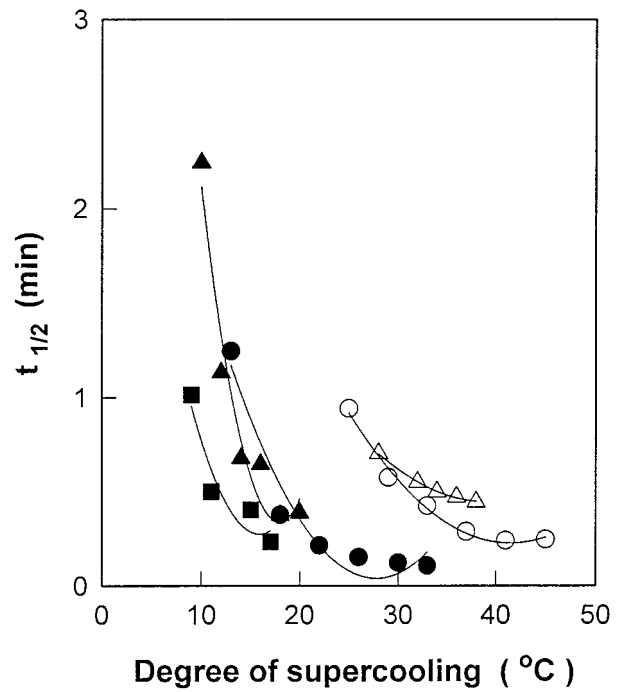


Figure 6 Crystallization behavior of various PPADs: (●) PP2; (○) PP3; (▲) PP4; (△) PP5; (■) PP6.

to more flexible chains, crystallize more readily. The longer aliphatic units in PPADs, the higher the crystallization rates. An odd-even effect is

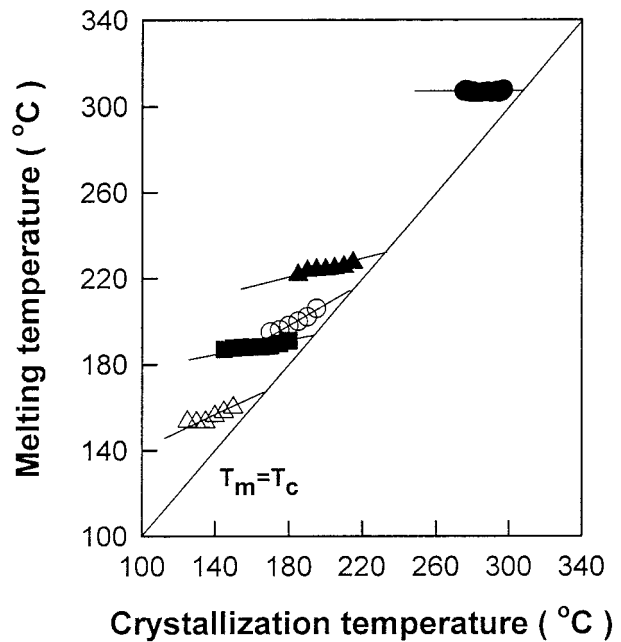


Figure 7 Determination of the equilibrium melting temperature T_m^0 for various PPADs: (●) PP2; (○) PP3; (▲) PP4; (△) PP5; (■) PP6.

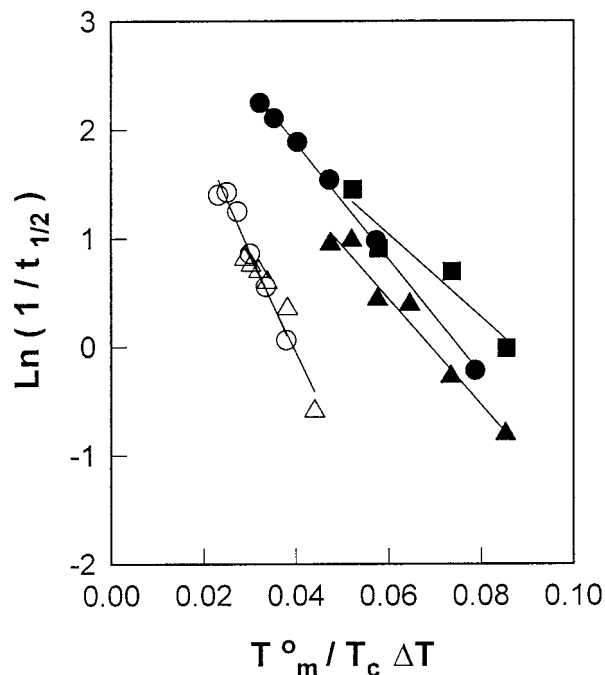


Figure 8 Plots of $\ln(1/t_{1/2})$ versus $T_m/T_c\Delta T$ for various PPADs: (●) PP2; (○) PP3; (▲) PP4; (△) PP5; (■) PP6.

also observed in K_2 and K_3 , as observed in the melting temperatures of PPADs. PPADs with an even number of carbon atoms crystallize faster than do PPADs with an odd number of carbon atoms. The odd–even number effect in the crystallization behaviors of PPADs may be explained by the molecular symmetry of PPADs.²⁰ In the case of PPADs with an even number of carbons, they have centers of symmetry at the centers of the benzene rings and at the middle of the central methylene bond in the chemical repeating unit. On the other hand, PPADs with an odd number of carbons have the centers of symmetry only at the centers of the benzene rings. As a result, in the crystallization of PP3 and PP5, it is much less probable for chains to be incorporated into a crystal order when the chains approach the crystal surface. However, further study on the exact crystallographic structure of crystallized polymers is needed to establish solid relationships between the chemical structure and the crystallization behavior.

CONCLUSIONS

Several PPADs with a different length of aliphatic unit were synthesized and their crystallization

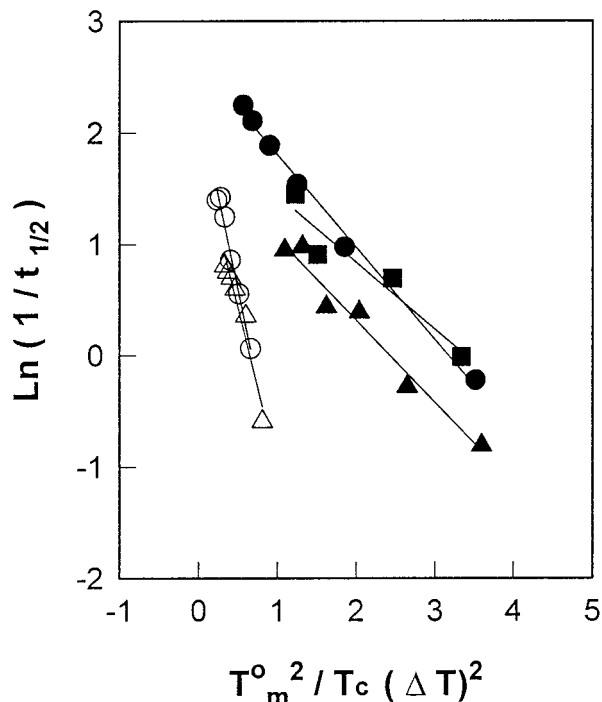


Figure 9 Plots of $\ln(1/t_{1/2})$ versus $T_m^2/T_c(\Delta T)^2$ for various PPADs: (●) PP2; (○) PP3; (▲) PP4; (△) PP5; (■) PP6.

behaviors were examined. The melting temperatures of PPADs decrease with increase in the length of aliphatic unit. An odd–even effect on the melting temperatures of PPADs was also observed. Isothermal crystallization kinetics of PATs and PPADs were analyzed by using the Avrami equation and compared to each other. PPADs crystallize more readily than do PATs. In a series of PPADs, PPADs with the longer aliphatic units crystallize faster than do those with the shorter aliphatic units, and an odd–even effect is observed. Higher crystallization rates of PPADs with longer aliphatic units are due to the increased flexibility of polymer chains, and lower crystallization rates of PPADs with an odd num-

Table IV Kinetic Parameters of Various PPADs

Polymer	K_2 (K)	K_3 (K)
PP2	53.23	0.83
PP3	96.69	3.38
PP4	48.89	0.74
PP5	88.51	2.88
PP6	38.18	0.60

ber of carbons may be a result of the fact that there are fewer centers of symmetry in the chain as compared with PPADs.

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