Table 1 Thermal transitions

Diiso-cyanate	Hard segments (wt %)	First heating cycle		Second heating cycle	
		T_g[b] (°C)	Endotherms (°C)	T_g[b] (°C)	Endotherms (°C)
TDI	32	–16	43 (Very small)	–21	None
HDI	32	–42	42 (Sharp, medium strength) 156 (Sharp, strong)	–46 (Very sharp)	32 (Medium strength) 156 (Sharp, strong)
H_{12}MDI	40	–39	52 (Small) 80 (Small) 130 (Sharp, strong)	–43 (Sharp)	66 (Broad 132 (Sharp, strong)
IPDI	36	–32 to –35	51 (Broad, very strong)	–37	38 (Strong)
MDI[a]	39	~–31	~205 (Sharp, strong)	~–31	~205 (Sharp, strong)

[a] The elastomer based on MDI was prepared by injection moulding, not solvent casting.
[b] T_g as indicated by the onset of the transition

an endotherm above 100°C, though it cannot be taken as proof of the absence of a separate hard segment phase, indicates that if such a phase exists the binding forces are weak.

HDI- and H_{12}MDI-based elastomers

The much lower T_g found in these elastomers compared with the MDI based equivalent point to more complete phase separation than in the latter. Both provide evidence of the existence of a separate hard segment phase in the endotherms noted above 100°C. The presence of a separate soft segment phase is further indicated in the HDI-based material by the endotherm noted below 100°C. As with the TDI-based elastomer an endotherm below 100°C appeared in the H_{12}MDI-based sample only in the sample aged for 3 years. We offer no explanation of the endotherm noted below 100°C in the latter elastomer but above the melting point of the soft segment (~54°C).

IDPI-based elastomer

Judged by its T_g the IPDI-based elastomer appears to show better phase separation than the MDI-based equivalent. There is evidence for the existence of a relatively pure soft segment phase in the endotherm noted below 100°C. As with the TDI-based elastomer, the absence of an endotherm above 100°C is not proof of the absence of a hard segment phase but again indicates weak binding forces if a hard segment phase exists.

The results obtained in this study indicate a much stronger tendency for aliphatic diisocyanate-based urethane thermoplastic elastomers to exist in two phases than do aromatic diisocyanate-based equivalents. Surprisingly this occurs even when an unsymmetrical aliphatic diisocyanate is used and therefore in the absence of the driving force in phase separation involving the tendency of the hard segments to form crystallites. We conclude that the main driving force leading to improved phase separation in the aliphatic diisocyanate based materials is connected with the greater strength of hydrogen bonds formed from aliphatic diisocyanate derived urethane groups and/or the different polarities. The greater flexibility of segments derived from aliphatic diisocyanates may also contribute to the effect in that they are less liable to be trapped in the soft segment and held there by ester/urethane hydrogen bonds.

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Effect of photodegradation on the rate of spherulitic growth of poly(ethylene glycol adipate)

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INTRODUCTION

The effect of degradation on the rate of crystallization of polymers has received little attention. Polymer degradation generally results in one or several of the following main effects: crosslinking, main chain scission and side chain scission sometimes accompanied by unsaturation formation[1].

The present study concerns the rate of growth of spherulites in poly(ethylene glycol adipate) (PEGA) irradiated at room temperature in air, either pure or in the presence of benzophenone, with u.v. light of wavelength 253.7 nm. Crosslinks are formed in the polymer in both cases.

The rate of crystallization of the undegraded polymer has been thoroughly investigated by numerous authors owing to the large size of the formed spherulites, their easily observable growth rate and their interesting morphology[2–4]. Three major structures of spherulites have been identified between 15° and 50°C by polarizing optical microscopy, X-ray diffraction and calorimetry, but their regime of crystallization has not been determined.

EXPERIMENTAL

The polymer was prepared by condensation of adipic acid and ethylene glycol in decalin at 150°C in the presence of *para*-toluenesulphonic acid[5]. It was purified by successive dissolutions in acetone followed by precipitation in methanol. The molecular weight was shown to be ~3000 by g.p.c. Films 10 μm thick were cast from CH_2Cl_2 on microscope slides and the solvent evacuated under vacuum. The rate of growth was measured with a polarizing microscope. Irradiations were performed at room temperature in air with a Phillips TUV 15 W low pressure mercury lamp at a distance of 23 cm from the sample. The incident intensity at this distance is $\sim 3 \times 10^{-8}$ E/min/cm^2. After irradiation the samples were heated to 85°C before studying the crystallization at different temperatures.

RESULTS AND DISCUSSION

The formation of crosslinks during irradiation of PEGA was demonstrated by the presence of an insoluble gel in the samples used to study the spherulitic growth rate. In less irradiated samples, the gel point of which is not attained, the molecular weight distribution was shown by g.p.c. to be continuously displaced to higher molecular weights, in agreement with the theories of crosslinking[6].

The spherulite growth rate was studied at 5 temperatures: 23°, 30°, 35°, 40° and 45°C. At 23° and 30°C, the well known ringed spherulites are observed while at higher temperatures spherulites with positive birefringence are formed. The low temperature modification with negative birefringence was observed below 23°C but its rate of growth was not studied in the present work. The morphology of the spherulites obtained at a given temperature is not altered by degradation as far as it can be observed by optical microscopy.

Nucleation is heterogeneous; indeed, the spherulites appear simultaneously and the nucleation frequency is dependent on the thermal history of the sample. Annealing of the samples at 85°C (i.e. ~31°C above the melting point) is necessary to destroy the nucleation centres. An induction period was usually observed at temperatures higher than 35°C. The rate of growth as a function of time is constant up to collapse of the spherulites. The spherulitic growth rate is given in *Table 1* for irradiated and non-irradiated samples. It is lower for the irradiated samples and decreases with the irradiation time in both conditions of degradation studied (pure samples or samples containing benzophenone as sensitizer).

Table 1 Rate of radial growth of PEGA spherulites (μm/min)

Crystallization temperature (°C)	Non-irradiated sample	Irradiation time (irradiated samples without additive)			Irradiation time (irradiated samples containing benzophenone)	
		9 h	15 h	20 h	9 h	20 h
23	12.5	11	–	–	8	2.1
30	6	5	–	–	5	1.1
35	4.4	2.3	–	–	2.5	0.47
40	2.2	1.6	–	0.6	1.3	0.3
45	1	0.7	0.4	0.2	0.06	0.02

In general, crystallization can be analysed using the Turnbull–Fisher equation[7] that applies to the radial rate of growth of spherulites in the case of nucleation controlled crystallization and has been generalized recently by Lauritzen and Hoffmann[8,9]:

$$G = G_0 \exp\left[-U^*/R(T - T_\infty)\right] \times \exp\left[-K_g/T(\Delta T)f\right] \qquad (1)$$

The factor G_0 is a constant that governs the absolute rate of crystal growth and depends on the regime of crystallization. (Regime I signifies that a single surface nucleus leads to completion of the substrate while in regime II, numerous surface nuclei are involved in substrate completion.) The first exponential factor is the transport factor. It is responsible for the rate increase with increasing temperature usually observed for G at high undercooling. The values of $U^* = 1500 \pm 200$ cal and $T_\infty = T_g - 30$°C were found to fit the data for most linear polymers. The second factor gives the probability of formation of a nucleus of critical size. It is responsible for the decrease of the rate of crystallization as the temperature increases, usually reported at low undercooling and also observed in the present work as indicated by the results of *Table 1*. The value of ΔT is $T_m^0 - T$ and K_g is given by:

$$K_g = Y\sigma_u\sigma_e T_m^0/(\Delta h_f)k$$

where T_m^0 is the equilibrium melting temperature relevant to the molecular weight under consideration, Y is 4 (for regime I) or 2 (for regime II), σ_u and σ_e are the surface free energies, parallel and perpendicular to chain direction, respectively, and f is a factor close to unity.

According to data previously reported in the literature, crosslinking is most certainly responsible for the variation of many parameters in equation (1). Indeed, G_0 was shown to depend on the regime of crystallization and, in each regime, on the *MW*. For polyethylene of very low *MW* at low undercooling (regime I) it increases with *MW*, but for higher *MW* and regime II, the reverse effect is reported[9]. The effect of crosslinking on G_0 has not been reported.

The form of the transport factor given in equation (1) is verified for linear polymers. Another expression of it is useful to predict its variation with crosslinking; this expression has been proposed previously by Hoffmann[10] and corresponds to the relation of Williams, Landel and Ferry[11]. According to this, the first exponential factor in equation (1) has to be replaced by $\exp[C_1/R(C_2 + T - T_g)]$. The glass transition temperature is known to increase with *MW* in the low *MW* range. It increases with crosslinking density when the distance between crosslinks is shorter than the segment responsible for molecular relaxation at T_g[12]. Such an increase of T_g leads to a decay of the transport factor.

The effect of *MW* on the nucleation factor is more complex. The variation of σ_e is intricate. Data on monodisperse samples discussed according to equation (1) indicate[9] that it increases with *MW* for low *MW* samples but is fairly constant above 20 000. Increasing the *MW* raises the equilibrium melting temperature in the low *MW* range but crosslinking has the reverse effect. This last displacement is however not very large when the crosslinks are formed in crystalline samples as in the present case[13]. A decrease of the melting temperature would yield a reduction in the nucleation factor as does the increase of σ_e.

This discussion shows that an increase of *MW* and crosslinking density could affect the spherulitic rate of growth through the variation of many parameters.

Assignment of the decreased rate of growth observed in the present work, to one or more of these parameters would however be very difficult in the case of PEGA since each type of spherulite can only be studied in a narrow temperature range and so many parameters have to be determined as a function of *MW* and crosslinking density.

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Solution properties and chain flexibility of poly(2-chlorophenyl methacrylate)

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As a part of our investigation programme about poly(methacrylic esters), we present here some results obtained for poly(2-chlorophenyl methacrylate) which are compared with those found for poly(phenyl methacrylate)[1] and other poly(chlorophenyl methacrylates)[2,3] in order to test the effect of the hydrogen–chlorine substitution on the solution properties and the chain flexibility.

Nine fractions of $\bar{M}_w$ from 6.7 x 10^4 to 74 x 10^4 were prepared and characterized in the way already described for other poly(methacrylic esters)[1,4]. Mark–Houwink constants, interaction parameters B of Stockmayer–Fixman relation, K_θ value and chain flexibility factor σ derived from viscosity measurements are collected in *Table 1*. The average value of K_θ corrected for polydispersity was obtained as previously[5] using the extrapolation methods proposed by Stockmayer–Fixman, Kurata–Stockmayer, Cowie, Kamide–Moore and Inagaki–Kurata. Adopting for the Flory constant ϕ the value of 2.87 x 10^{21}, we found the relation between the unperturbed dimension and molecular weight as:

$$\langle \overline{r_0^2} \rangle^{1/2} = 0.50M^{1/2} (\text{Å})$$

The flexibility factor σ was calculated taking a freely rotating chain dimension $\langle \overline{r_{0f}^2} \rangle^{1/2}$ of $0.22M^{1/2}$. The reported value is relatively low for a poly (methacrylic ester) having an aromatic side chain[5].

The preceding constants can be compared in *Table 1* with the corresponding values found for poly(phenyl methacrylate) and other poly(chlorophenyl methacrylates). More accurate σ values than those previously report-

Table 1 Mark–Houwink constants, interaction parameter B of Stockmayer–Fixman relation, K_θ average value and chain flexibility factor σ for poly(phenyl methacrylate) and poly(chlorophenyl methacrylates)

	Mark–Houwink constants				
Polymer–solvent	$K_a \times 10^3$ (cm^3/g)	a	$B \times 10^{28}$ (cm^3 g^{-2} mol^2)	$K_\theta \times 10^3$ (cm^3/g)	σ
Poly(2-chlorophenyl methacrylate):					
Tetrahydrofuran	3.2	0.74	–		
Dioxane	8.3	0.64	2.2	36	2.27
Benzene	9.33	0.62_5	1.5		
Toluene	41.9	0.45	–		
Poly(phenyl methacrylate)[1]:					
Dioxane	5.42	0.73	7.8	59	2.46
Benzene	5.75	0.72	6.4		
Poly(4-chlorophenyl methacrylate)[2]:					
Dioxane	6.1	0.70	3.45	48	2.50
Benzene	9.2	0.66	2.70		
Poly(2,4,5-trichlorophenyl methacrylate)[3]:					
Dioxane	11.8	0.58	1.0	26	2.37
Benzene	21.2	0.51_5	~0.0		