Differential scanning calorimetry of some well defined poly(ε-caprolactone-*g*-PMMA)-*co*-polyurethanes

S. Rimmer and M. H. George*
Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AZ, UK

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The thermal behaviour of a series of well defined segmented polyurethanes (PU) grafted with poly(methyl methacrylate) (PMMA) has been examined using differential scanning calorimetry. The grafts were located only in the poly(ε-caprolactone) (PCL) soft segments. Three annealing schedules were employed. Grafting was found to have little effect on the hard segment domains, provided the hard segments were long enough to crystallize. Phase separation of the PCL and PMMA was incomplete. A transition, which was shifted to higher temperatures as the annealing temperature increased, was assigned to the glass transition (T_g) of a PCL/PMMA mixed amorphous phase. PCL crystalline melting and a PCL T_g were observed in the polymers with a low concentration of PMMA; an event which could be assigned to the T_g of a PMMA phase was not detected in any of the samples.

(Keywords: polyurethane; poly(ε-caprolactone); poly(methyl methacrylate))

INTRODUCTION

The morphology of linear segmented polyurethanes (PU) has been studied by several authors. Reviews which cover the work up to 1981 have been published by Gibson *et al.*[1] and Chang *et al.*[2]. Differential scanning calorimetry (d.s.c.) has played an important role in these studies. The results of a d.s.c. study on PUs grafted with poly(methyl methacrylate) in the soft segments are reported in this work.

In general the lowest temperature thermal event observed is due to the soft segment glass transition, T_g. D.s.c. studies on PUs where poly(ε-caprolactone) (PCL) forms the soft segment have been published. Hesketh *et al.*[3] studied PUs with PCL soft segments and hard segments formed from the reaction of 4,4′-diphenylmethanediisocyanate (MDI) or 4,4′-dicyclohexylmethanediisocyanate (H_{12}MDI) and 1,4-butanediol (BD). In the MDI materials a PCL molecular weight of at least 2000 was required for soft segment crystallization to be observed. Soft segment crystallization was not observed in any of the H_{12}MDI materials.

Three transitions which are highly susceptible to thermal history are often observed in PUs. Of these events, the one of lowest transition temperature (I) often occurs 20–50°C above the annealing temperature. The second (II) occurs at 120–190°C and the final thermal event (III) may be seen as an endothermic peak in excess of 200°C. These transitions have been assigned to the breakup of domains of varying degrees of order[4–6]. Several workers[1,7–9] have studied annealing-induced morphological changes in these materials. Upon annealing, transition I shifts in a continuous manner until it merges with II. This behaviour has been taken as evidence of improvements in short-range ordering. Transition II can similarly be shifted into region III provided the hard segments are of sufficient length to crystallize. The crystalline melting peak (III) has been shown to be independent of annealing temperature, unless severe temperatures are used[3,10]. Bogart *et al.*[7] studied PUs with soft segments of either PCL, poly(tetramethylene adipate) or poly(tetramethylene oxide). In most materials a type I transition was seen. In those materials which exhibited soft segment and hard segment crystallinity the magnitude of this event was much reduced and in some cases unobservable. The same group[11] helped to show that increasing the hard segment length of PCL-containing PUs had the effect of increasing the size and position of the transition III peak. A study of PUs with PCL soft segments by Chang and Thomas[2], showed the presence of well developed hard segment crystallinity only in polymers that were bulk crystallized. These samples did not show soft segment crystalline melting, whereas samples cast into films did.

Leung and Kobertson[9] have introduced the concept of microphase separation (MST). This is the temperature at which separation from the homogeneous state occurs. They have assigned event II, described above, to this process.

Akcelrud and Gomes[12] studied PMMA-*g*-PU materials, in which the PU component was linked to the PMMA backbone by a single toluene diisocyanate unit. They reported the observation of transitions at the PMMA T_g,

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* To whom correspondence should be addressed

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the macroglycol T_g and a new transition between these events. The latter were shifted to higher temperatures when further d.s.c. runs were performed on the samples. They postulated that these transitions were due to the phase separation of a mixed PU/PMMA. Wilson[13] synthesized hard segment unsaturated PUs and then copolymerized these with MMA. The macroglycol and PMMA T_gs were seen in the d.s.c. traces and once again a new transition was observed which lay between the two T_gs.

Much d.s.c. work has been carried out on interpenetrating network (IPN) materials. In the PU/PMMA IPNs of Kim *et al.*[14–16] no events that could be attributed to the T_g of a mixed PCL/PMMA phase were seen. However, small inward shifts of the PMMA and PCL T_gs were observed. This phenomenon was attributed to mixing at phase boundaries.

In a recent work[17] the authors reported the synthesis of PU-*g*-PMMA materials, by a route which allowed graft copolymers of well defined architecture to be synthesized. In this and subsequent publications, the morphology and structure/property relationships of these materials will be examined.

EXPERIMENTAL

Materials

The PU-*g*-PMMAs were synthesized by the method outlined in our previous publication[17]. The hard segments are formed from the reaction of MDI with BD. In brief, these materials were synthesized by preparing a 1,2-diol PMMA macromonomer. This material was then reacted with ε-caprolactone in a ring-opening polytransesterification to produce a PCL-*g*-PMMA macrodiol. In order to produce grafted PUs with predetermined degrees of soft segment grafting, the PCL-*g*-PMMA is blended with a linear PCL diol. The PCL-*g*-PMMA/PCL blend or PCL-*g*-PMMA is then chain extended with BD and MDI to yield the segmented PUs with PMMA grafts in the soft segments.

The PU-*g*-PMMAs have been given a nomenclature of the following form: *x*/*y*/*z*, where *x* denotes the weight percentage of hard segment in the PU, *y* is the number-average molecular weight of the PMMA side chains and *z* is the weight percentage of PMMA in the polymer. The homo PUs have been named as PU*x*, where *x* is the weight percentage of hard segment.

D.s.c. has also been carried out on the PCL-*g*-PMMAs and the homo PCL and PMMA polymers used to synthesize the PU-*g*-PMMA materials[17]. Two PMMA polymers were used; these have been designated PMMA 850 and PMMA 12000, where the numbers are the number-average molecular weights of the PMMA. Similarly, the PCL-*g*-PMMA polymers have been identified as PCL-*g*-PMMA 850 and PCL-*g*-PMMA 12000. The weight fraction of PCL in these PCL-*g*-PMMA diols is 0.71 and 0.13, respectively. The molecular weight of the PCL segment in all of these materials was[17] ~2000.

D.s.c.

D.s.c. was used to examine the thermal behaviour of the grafted and linear PUs, the linear and grafted PCLs and the homo PCL and PMMA polymers. A Dupont 9000 machine was used. Approximately 20 mg of sample was accurately weighed into an aluminium d.s.c. pan. The sample pan was sealed and placed, along with an empty reference pan, in the d.s.c. cell. The liquid nitrogen cooling assembly was put in place. The cell was cooled to −120°C and heating commenced at a rate of 10°C min^{-1}. This part of the run was continued up to 40°C. The cell was then cooled to 0°C, the cooling assembly removed and heating, up to 265°C, commenced. Indium was used to calibrate the temperature scale of the instrument. An inert gas purge was not used. The errors in the temperature measurements are estimated as ±2°C.

Three annealing schedules were used in order to study the effect of thermal history on PU relaxation behaviour. The samples were annealed at either 50, 80 or 120°C for 24 h, in a vacuum oven. On removal from the oven, the samples were allowed to cool slowly on the bench. Typically the d.s.c. analysis was carried out 30 min after removal from the oven. All the other materials were tested after drying the precipitated polymer at 50°C in a vacuum oven.

RESULTS AND DISCUSSION

D.s.c. of the PU polymers

The thermal properties of PUs are strongly dependent on the thermal history of the samples. Therefore, the thermal history of all the grafted and linear samples was controlled by annealing at three different temperatures prior to testing.

In the PUs four events are observed. These are labelled α, β, γ and δ on going from high to low temperature. The α- and γ-transitions are observed as first-order transitions, whereas β- and δ-transitions give rise to second-order transitions in the form of baseline gradient changes. The β-transition is not observed in the PU homopolymers but is present in the grafted copolymers, and is therefore associated with the grafted PMMA chains. Many of these d.s.c. curves show evidence of degradation above 200°C. This is observed as a steadily rising baseline. In the 50% hard segment series, the α-transition occurs in the same region as the degradation and therefore some of the curves are complicated by this feature.

Some examples of the d.s.c. curves obtained in this work are shown in *Figures 1–3*. All of the transition temperatures are shown in *Tables 1* to *3*. The temperatures of second-order transitions which occur as changes in baseline slope are quoted as the temperature of the onset of the transition. For endotherms which occur as peaks, the onset and end temperatures are quoted and the peak

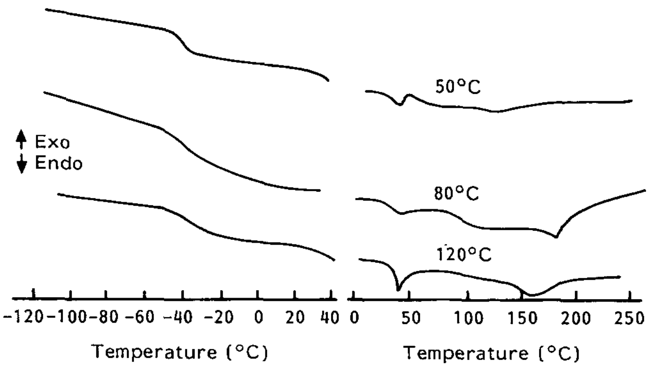

Figure 1 D.s.c. curves of PU-*g*-PMMA 30/12000/25, annealed at 50, 80 and 120°C

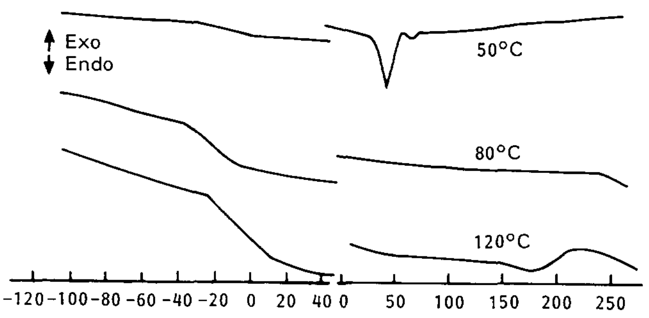

Figure 2 D.s.c. curves of PU-*g*-PMMA 30/850/50, annealed at 50, 80 and 120°C

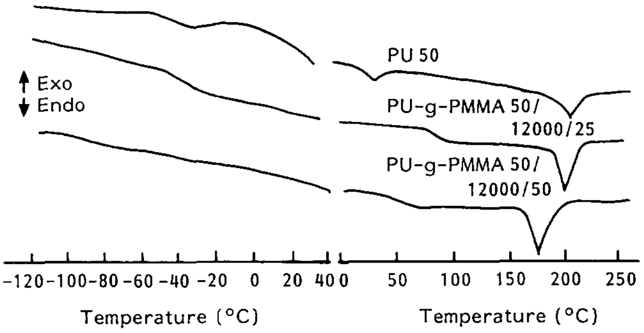

Figure 3 D.s.c. curves of the 50% hard segment series annealed at 50°C

Table 1 D.s.c. results of the linear PUs

Sample ref.	Annealing temperature (°C)	Transition temperature (°C) δ	γ	β	α
PU30	50	−58	20–70(40)	–	125–180
	80	−58	20–70(42)	–	125–180
	120	−58	20–55(42)	–	160–180
PU50	50	−55	10–42(30)	–	175–235(205)
	80	−55	–	–	170–220(200)
	120	−55	–	–	180–230(205)

Values in parentheses are peak temperatures

Table 2 D.s.c. results for the grafted PUs of 30% hard segment content

Sample ref.	Annealing temperature (°C)	Transition temperature (°C) δ	γ	β	α
30/12000/25	50	−50	20–45(40)	50	110–120
	80	−50	27–47(40)	80	150–180
	120	−50	31–46(39)	–	140–180
30/12000/50	50	−45	–	62	–
	80	−45	–	95	–
	120	−45	–	100	–
30/850/25	50	–	25–48(40)	−35	–
	80	–	–	−35	–
	120	–	–	−25	150–200

Values in parentheses are peak temperatures

temperature is shown in parentheses. *Table 4* shows the percentage of PCL chains which are grafted for a given composition and the estimated T_g which would be observed if the PMMA and PCL existed as a homogeneous blend. These T_gs were calculated using the Fox equation:

$$1/T_g = W_a/T_{g_a} + W_b/T_{g_b} \tag{1}$$

T_g, T_{g_a}, T_{g_b} are the glass transition temperatures of the mixture and of the homopolymers a and b. W_a and W_b are weight fractions of the homopolymers a and b. Values of −62°C for the T_g of PCL and 118°C (PMMA 12000) or 62°C (PMMA 850) for the PMMA T_g were used.

Amorphous transitions β and δ

The lowest temperature transitions seen in these materials, δ, can be assigned to the T_g of the amorphous PCL phase. In the homo PUs (*Table 1*) T_δ shows an increase with increasing hard segment content which indicates the presence of a degree of mixing between hard and soft blocks. This type of behaviour is well documented in the literature on polyester PUs[1].

Tables 2 and *3* show the effects of grafting PMMA of $M_n = 12\,000$. The effects of grafting the 30% hard segment series of polymers are illustrated in *Table 2*. T_δ increases as the PMMA content of the copolymer increases. No change in T_δ is observed with changing thermal history. In the 50% hard segment materials (*Table 3*) δ is seen in the linear polymer and the most lightly grafted material (PU-*g*-PMMA 50/12000/25). As in the 30% hard segment series, T_δ is raised in the grafted polymer and is unaffected by annealing, The behaviour of δ is discussed further below.

The absence of a transition that could be assigned to a PMMA homophase points to the hypothesis that β is due to a mixed amorphous phase which contains varying amounts of PMMA, PCL and some entrapped hard segment. In general these transition temperatures are well removed from the values predicted by the Fox equation, for homogeneous mixing of all the PMMA and PCL (*Table 5*). T_β increases with increasing annealing temperature. An explanation for this behaviour is that the mixed state consists of PMMA mixed with the PCL which is directly linked to the PMMA plus some of the adjacent PCL segments, so that some of the PCL is forced into mixing with the PMMA side chains. However,

Table 3 D.s.c. results for the grafted PUs of 50% hard segment content

Sample ref.	Annealing temperature (°C)	Transition temperature (°C) δ	γ	β	α
50/12000/25	50	−50	–	75	180–210(200)
	80	−50	–	125	180–220(200)
	120	−50	–	155	180–220(205)
50/12000/50	50	–	–	35	160–200(175)
	80	–	–	100	180–210(190)
	120	–	–	100	180–210(190)

Values in parentheses are peak temperatures

Table 4 Fraction of PCL chains which are grafted and values of T_g calculated using the Fox equation

Sample ref.	Fraction of PCL chains grafted	Calculated T_g (°C)
30/12000/25	0.08	−25
30/12000/50	0.23	16
50/12000/25	0.11	−14
50/12000/50	0.30	35
30/850/25	1.00	−34

the maximum T_β attained (155°C in PU-*g*-PMMA 50/12000/25) is well above the T_g of the homo PMMA component, so that it can be concluded that the β-phase must also contain mixed-in hard segments.

The behaviour of the β-transition on annealing may be related to changes in hard segment domain structure since in most of these materials annealing has the effect of increasing the degree of ordering in the hard segment domains. This is observed as increases in T_β with annealing temperature. An alternative explanation may be that annealing produces compositional changes within this phase. At the moment the increase in T_β with annealing temperature cannot be satisfactorily explained and further studies are required to elucidate this behaviour.

In PU-*g*-PMMA 50/12000/50 T_δ and T_β no longer appear as resolvable transitions but are merged into a single thermal event. This transition is clearly dependent on thermal history so that the authors have classed it with the β-transitions above. A similar result is observed in the material PU-*g*-PMMA 30/850/25 (i.e. β and δ are merged).

It would appear from these results that a critical degree of grafting of the PCL component exists above which δ and β are merged. By reference to *Table 4* it can be seen that the critical fraction of grafted PCL polymer chains lies between 0.23 and 0.30. Above this range δ and β are merged.

The γ-transition

This endotherm is due to the melting of a crystalline PCL phase. Both the linear polymers show this transition. Soft segment crystallinity in PU50 is easily removed by annealing, whereas in PU30 it persists even after annealing at 120°C. These observations are well documented in the literature[1]. Grafting has a profound effect on this transition. In most of the samples grafting inhibits PCL crystallinity to such an extent that a δ endotherm is not seen. Also in the samples where PCL melting is seen, the transition temperature is reduced, which indicates the formation of less perfect crystals. Aladesulu *et al.*[18] also reported a decrease in crystallinity when poly(methyl methacrylate) was guest polymerized within a PU network and where some of the poly(ethylene glycol) soft segments may have been grafted.

The behaviour of 30/850/25 and 30/12000/25 materials provides a comparison of the effect of grafting with many small chains or with fewer larger chains, while the overall fraction of PMMA is kept constant. In the copolymer with less than 1% of the PCL chains grafted, 30/12000/25, the soft segments were able to crystallize to a significant degree. PCL crystalline melting can be observed for all annealing schedules in this sample. In the 30/850/25 material it would appear that PCL crystallites are able to form to a limited degree. However, the crystallinity is easily removed by annealing.

The α-transitions

The 30% hard segment content PU displays a broad endotherm above 120°C, which is strongly affected by annealing above 80°C. This PU has hard segment blocks, which are too short to crystallize but can form regions which are intermediate in order between the fully disordered, amorphous state and the crystalline state. Annealing increases the degree of order in these domains. As the perfection in the packing of the hard segments increases, the temperature at which the domains break up increases, so that at a given annealing temperature, the hard segments rearrange into domains of a degree of order which is greater than that which would dissociate below the annealing temperature. The crystalline regions in PU50 melt at temperatures too far above the highest annealing temperature to be affected by annealing at this temperature. Grafting has little effect on the crystalline melting observed in the PU50 series. However, the change in behaviour of the PU30 series materials with grafting, suggests that hard segment domains, which are not crystalline, are disrupted by the PMMA grafts.

D.s.c. of the precursors

D.s.c. was performed on PCL and PMMA homopolymers and the PCL-*g*-PMMA polymers. The results are tabulated in *Table 5*, and *Figures 2–6* show the d.s.c. curves of these materials.

The behaviour of the PCL and PMMA homopolymers is typical for these polymers. A single T_g is observed in the PCL-*g*-PMMA 12000 material. Although the observed temperature differs from the value calculated using the Fox equation (80°C) it can still be implied that in this material the PCL and PMMA segments are homogeneously mixed. The d.s.c. of PCL-*g*-PMMA 850 exhibits a sharp crystalline melting. It is also reasonable to expect that an endotherm arising from a T_g of the amorphous region would be observed in this material.

Table 5 D.s.c. results of the precursors

Sample ref.	T_g (°C)	T_m (°C)
PMMA (M_n=850)	62	–
PMMA (M_n=12000)	118	–
PCL-*g*-PMMA 850	–	45–65(58)
PCL-*g*-PMMA 12000	105	–
PCL	−62	20–40(30), 40–60(50)

Values in parentheses are peak temperatures

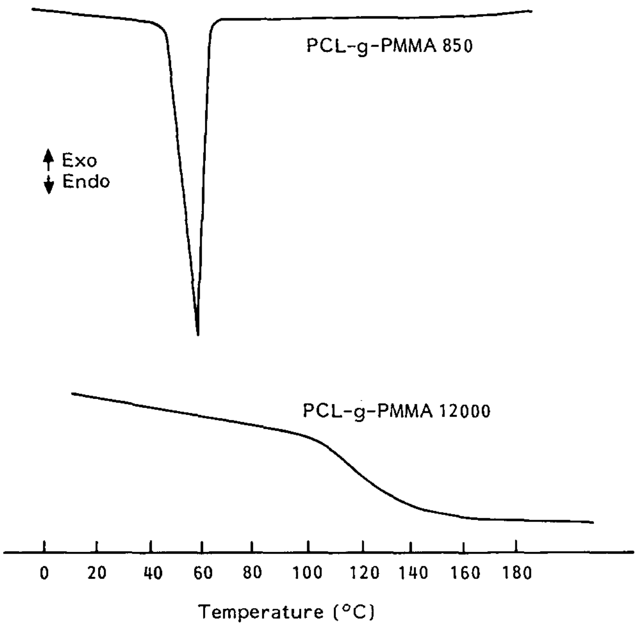

Figure 4 D.s.c. curves of the PCL-*g*-PMMA series

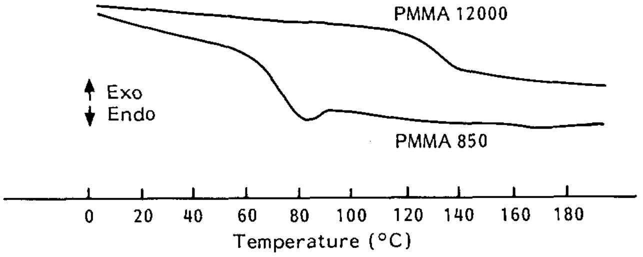

Figure 5 D.s.c. curves of the PMMA macromonomers

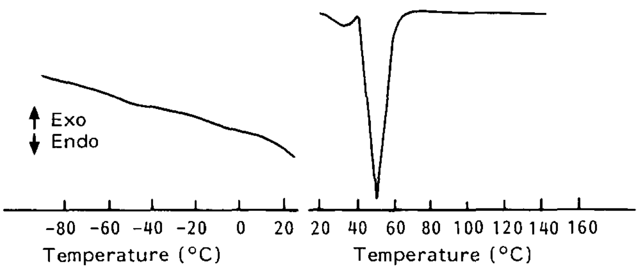

Figure 6 D.s.c. curves of the PCL homopolymer

Such an event was not visible in the d.s.c. trace. However, it is unlikely that the PMMA side chain could be incorporated into the PCL crystalline phase, therefore the amorphous T_g is probably located in the same temperature region as the melting transition and is obscured by the latter event.

An additional feature of the PCL-*g*-PMMA 850 trace is the fact that the melt temperature is shifted upwards compared to the linear PCL melt temperature. The reason for this result is at the moment unclear.

Discussion on changes in hard segment/soft segment miscibility

The increase in T_δ with PMMA content can be explained in several ways. First, the phase giving rise to the δ-transition may not be homogeneous, that is, mixing of PMMA and PCL may occur at phase boundaries. This has been shown to occur in PMMA/PU IPNs[14–16]. However, the increases in transition temperature seen in the current work are much larger than those seen in the IPNs. An alternative suggestion is that the presence of PMMA grafts increases the degree of mixing between the hard and soft blocks. This hypothesis is supported by changes in α with PMMA content. The α-transition in the 30% hard segment series arises from hard segment/soft segment phase separation on cooling from the homogeneous state. The temperature ranges are decreased slightly in the 25 wt% PMMA material while in the 50 wt% PMMA polymer α is not observed. Thus, it would appear that the degree of hard segment/soft segment phase separation does decrease with grafting. The α-transition in the 50% series is much less affected by the presence of grafts. In this series of materials the hard segments are long enough to crystallize. The effect of hard segment crystallinity on the thermal behaviour of these materials is best illustrated by reference to the 50 wt% PMMA polymers. In the PU-*g*-PMMA 30/12000/50 α is not observed, so that it can be assumed that very little hard segment domain formation is possible in this material. On increasing the hard segment length, while keeping the weight fraction of PMMA constant (i.e. PU-*g*-PMMA 50/12000/50), phase separation is observed. This is signified by the observation of α as the melting of hard segment crystalline domains. With these data in mind it must be expected that if an increase in phase mixing of the PCL and urethane components with increasing degree of grafting is a major factor in the increase in T_δ with increasing PMMA content, then it follows that the increase in T_δ with grafting should be larger for the materials with shorter hard segments. This phenomenon is indeed observed in the lightly grafted materials. Thus, in the 30% hard segment materials the attachment of 25 wt% PMMA to the linear backbone (i.e. comparison of PU-*g*-PMMA 30/12000/25 and PU30) increases T_δ by 18°C. In the analogous comparison in the 50% hard segment series (i.e. comparison of PU-*g*-PMMA 50/12000/25 and PU50) the increase is much smaller (5°C).

CONCLUSIONS

From the above discussion it is possible to propose a model of the morphology of these PU-*g*-PMMA polymers. Four phases can coexist, namely:

(1) A predominantly PCL phase exists which is increasingly interpenetrated by hard segments as the degree of grafting is increased.
(2) A crystalline PCL phase may exist. This phase is only found in graft copolymers with short hard segments (i.e. the 30% hard segment content materials) and low degrees of grafting, that is, in materials in which there is a relatively high density of PCL.
(3) An amorphous mixed PMMA/PCL hard segment phase is present in all of the materials. No evidence for a PMMA homo phase has been found.
(4) Crystalline hard segment domains are present in all those materials in which the hard segments are long enough to crystallize. In materials which contain non-crystallizable hard segments, these domains are only seen in the polymers which are lightly grafted.

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