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The effect of silicon and phosphorus on the degradation of poly(methyl methacrylate)

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Thermal decomposition of the polydimethylsiloxane-(azobiscyano-pentanoyl ester)s (PDMS-ACP) in the presence of methyl methacrylate (MMA) monomer yielded poly(dimethylsiloxane)-poly(methyl methacrylate) block copolymers (PDMS-*b*-PMMA). Phosphorus functionalized poly(methyl methacrylate) (DEVP-PMMA) was prepared by copolymerization of MMA with diethyl vinyl phosphonate (DEVP) with PDMS-ACP initiator. The thermal stability and apparent activation energy for thermal degradation of these copolymers were studied by thermogravimetry and compared with unmodified poly(methyl methacrylate) (PMMA). The incorporation of PDMS segments in block polymer improved thermal stability of PMMA, whereas phosphorylated PMMA displayed a lower thermal stability. The activation energies for the degradation process in PMMA and PDMS-*b*-PMMA, calculated by the Ozawa method, increased approximately with increase in conversion. The values of activation energy of phosphorylated PMMA were smaller than that of PMMA and decreased with increasing phosphorus content. Copyright © Elsevier Science Ltd.

(Keywords: phosphorylated; poly(methyl methacrylate); degradation)

INTRODUCTION

Poly(methyl methacrylate), PMMA, is an important thermoplastic material. However, PMMA is classified as slow burning, roughly comparable to wood in flammability and ignition characteristics. Therefore, thermal stability and flammability of PMMA is studied extensively[1,2]. Flammability of PMMA can be controlled to some extent by utilizing additive-type flame retardants[3–6] or by their structure modification[7–12].

The thermal property of PMMA has been investigated focusing on the effect of the introduced polydimethylsiloxane (PDMS) segments. It is reported that the incorporation of PDMS segment in block copolymers improved thermal stability of PMMA[13]. Moreover, the evident lack of tendency to carbonize on burning surface of the PDMS-*b*-PMMA copolymers is thought to be responsible for the lack of limiting oxygen index enhancement by PDMS segments in the PDMS-*b*-PMMA[14]. Recently, the microstructure and morphology of PDMS-*b*-PMMA block copolymers were investigated. The results indicated that block copolymers existed a phase modification[15]. Thereafter, the absolute kinetic parameters of polymerization for MMA photoinitiated with PDMS-ACP macroazoinitiator was evaluated. It was shown that the ratio of the rate constant for chain termination and chain initiation by primary radicals was higher in the case of PDMS-ACP compared to azobisisobutyronitrile (AIBN)[16].

On the other hand, the incorporation of diethyl vinyl phosphonate (DEVP) into PMMA has only a very small effect upon flame retardance[9]. However, the activation energy in thermal degradation of the DEVP-PMMA copolymers is not evaluated. Thermogravimetric analysis (t.g.a.) is widely used as a method to investigate the thermal decomposition of polymers and to determine the kinetic parameters[17,18]. In this paper, DEVP-PMMA copolymers are prepared by free-radical polymerization with macroazoinitiator PDMS-ACP. The thermal stability and apparent activation energy (E_a) in thermal degradation of the copolymers is studied by t.g.a.

EXPERIMENTAL

Polymerization

PDMS-ACP macroinitiators were prepared as described previously[13,15]. The number average molecular weight of the polysiloxane segments for PDMS$_b$-ACP, PDMS$_c$-ACP, and PDMS$_e$-ACP were 3000, 4100, and 7100, respectively[15]. The PDMS-*b*-PMMA polymers were characterized to be a block copolymer by spin–spin relaxation measurements[15].

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Table 1 Feed composition and phosphorus content of various polymers

Polymer[a]	MMA (g)	DEVP (g)	Initiator (g)	$\bar{M}_n(D)^b$ (10^4)	PDMS[c] (wt%)	Si[c] (wt%)	P^d (wt%)
PDMS$_b$-*b*-PMMA	6	0	2.08	4.5 (1.8)	10.7	4.1	–
PDMS$_c$-*b*-PMMA	6	0	1.88	5.9 (1.7)	15.8	6.0	–
PDMS$_e$-*b*-PMMA	6	0	2.10	10.6 (1.5)	19.3	7.3	–
DEVP$_b$-PMMA	6	3.4	0.50	9.7 (1.6)	4.5	1.7	1.6
DEVP$_c$-PMMA	6	3.4	0.76	9.6 (1.5)	7.5	2.8	1.0
DEVP$_e$-PMMA	6	3.4	1.24	8.1 (1.6)	16.8	6.3	0.9

[a] PDMS$_b$-*b*-PMMA = polydimethylsiloxane-poly(methyl methacrylate) block copolymer; initiated with PDMS$_b$-ACP initiator; DEVP$_c$-PMMA = phosphorylated PMMA initiated with PDMS$_c$-ACP initiator

[b] $\bar{M}_n$ = number average molecular weight calculated based on polystyrene standards by g.p.c. (numbers in parentheses indicate the molecular weight dispersity)

[c] PDMS = polydimethylsiloxane, calculated from ^{1}H n.m.r.

[d] P = phosphorus content

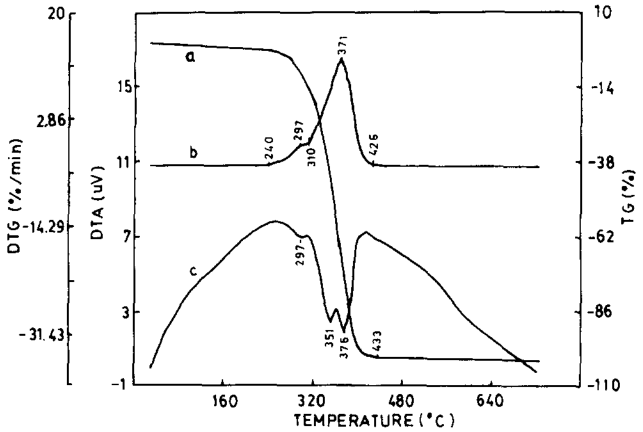

Figure 1 T.g.a. (a), d.t.g. (b), and d.t.a. (c) curves of sample PMMA at the heating rate 10°C min^{-1} under nitrogen atmosphere

DEVP-PMMA, phosphorus-containing copolymers, were prepared by free-radical copolymerization of monomer mixtures in toluene using macroinitiators PDMS-ACP. Feeds and experimental procedures in this work were similar to those of Banks[9]. The feed compositions and the phosphorus content of the copolymers are listed in *Table 1*. A typical reaction procedure is as follows. MMA (6.0 g, 0.06 mol), DEVP (3.4 g, 20.7 mmol; from Aldrich), PDMS$_c$-ACP (0.76 g) and dry toluene (100 ml) were introduced into a 300 ml three-necked flask equipped with a reflux condenser, connected with a calcium chloride tube, and connected by a gas inlet. The mixture was heated at 80°C for 32 h under a nitrogen atmosphere. Solvent was removed under reduced pressure and the viscous product was subsequently dropped into trichloromethane. The solution was dropped into a large amount of methanol to precipitate the polymer. The white precipitated polymer was filtered, washed with methanol (4×50 ml), and was dried in vacuum ($50°C \times 10$ h). Then, the DEVP$_c$-PMMA copolymer was obtained. Samples were designated so that, for example, DEVP$_c$-PMMA denotes a phosphorylated PMMA which is copolymerized of MMA with DEVP by use of PDMS$_c$-ACP initiator. In addition, the PMMA was prepared under the similar experimental conditions by reacting MMA with AIBN (0.010 M; from Merck) for the comparative purpose.

Characterization

The ^{1}H nuclear magnetic resonance (n.m.r.) spectra of the products in $CDCl_3$ were determined (Varian EM-390). Number-average molecular weight ($\bar{M}_n$) and molecular weight dispersity (D) of polymers were measured by gel permeation chromatography (g.p.c.) (Waters), with columns (Shodex KF 801 + 802 + 803 + 804), and tetrahydrofuran as eluent (1 ml min^{-1}). The phosphorus content of the synthesized copolymers was colorimetrically determined[19].

The characteristics and kinetics of degradation of copolymers was measured by Seiko SSC 5000 TG/DTA instrument. Heating rates of 5, 10, 20, and 40°C min^{-1} were used; the sample weight was about 10 mg, and the nitrogen flow rate was kept at 100 ml min^{-1}.

RESULTS AND DISCUSSION

Thermal analysis

PMMA prepared by free-radical polymerization, is known to begin degrading at approximately 175°C. The degradation originates from the formation of sterically hindered linkaged that result from head-to-head coupling during polymerization[19–22]. Unsaturated end groups that are formed by disproportionation during polymerization begin to degrade at 225°C, while the other possible saturated endgroups show to be thermally stable in a nitrogen atmosphere up to 300°C[23,24]. Random chain scission occurs above 300°C leading to depolymerization and monomer volatilization[25,26].

PMMA

Typical weight loss (t.g.a.), differential weight loss (d.t.g.) and differential thermal analysis (d.t.a.) curves of PMMA in this work ($\bar{M}_n = 292000$, $D = 1.7$) at a heating rate of 10°C min^{-1} under nitrogen are shown in *Figure 1*. The t.g.a. curve of PMMA indicates two main reaction stages (*Figure 1a*) which are reflected in two peaks in the d.t.g. curve (*Figure 1b*). The thermal decomposition of PMMA is accompanied by heat absorption as shown by the endothermic peak observed at its decomposition temperature (*Figure 1c*). The first reaction stage (240–310°C) and second reaction stage (310–430°C) were caused by end initiated[23,25] and random scission[25,26], respectively. The second part of the degradation shows two peaks (351°C and 376°C) in

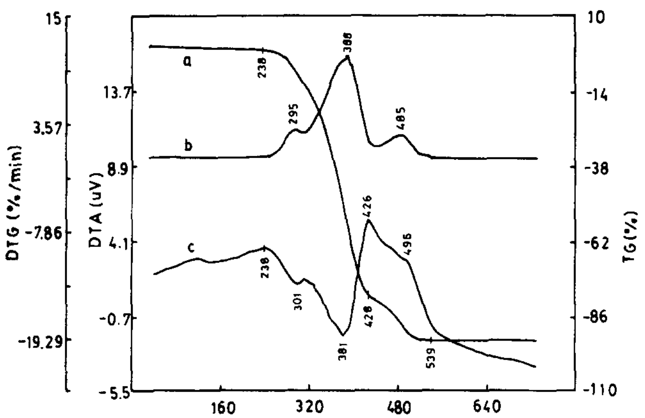

Figure 2 T.g.a. (a), d.t.g. (b), and d.t.a. (c) curves of sample $PDMS_c$-*b*-PMMA at the heating rate 10°C min^{-1} under nitrogen atmosphere

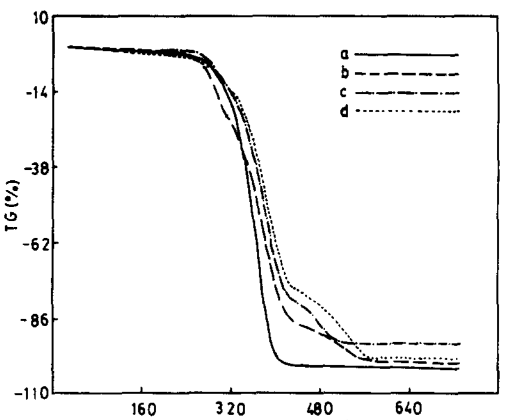

Figure 3 T.g.a. curves of sample PDMS-*b*-PMMA at the heating rate 10°C min^{-1} under nitrogen atmosphere: (a) PMMA, (b) $PDMS_b$-*b*-PMMA, (c) $PDMS_c$-*b*-PMMA, and (d) $PDMS_e$-*b*-PMMA

Table 2 Characteristic temperatures[a] on t.g.a. curves at 10°C min^{-1} heating rate under nitrogen atmosphere

Polymer[b]	T_{on} (°C)	T_{1m} (°C)	W_1^c (wt%)	T_{2m} (°C)	W_2^c (wt%)	T_{3m} (°C)	W_3^c (wt%)	Y_c^d (wt%)
PMMA	240	311	11.5	371	89.0	–	–	0.5
$PDMS_b$-*b*-PMMA	243	294	21.9	380	63.5	508	12.2	2.4
$PDMS_c$-*b*-PMMA	238	295	12.6	388	67.0	485	14.3	6.1
$PDMS_e$-*b*-PMMA	251	294	11.9	379	64.1	530	20.7	3.3
$DEVP_b$-PMMA	211	285	39.5	351	52.9	–	–	7.6
$DEVP_c$-PMMA	218	290	37.0	354	58.2	–	–	4.8
$DEVP_e$-PMMA	213	292	36.4	356	59.4	–	–	4.2

[a] The onset and maximum temperatures of the first step, T_{on} and T_{1m}, and the same for the second and third step, T_{2m}, T_{3m}

[b] $PDMS_b$-*b*-PMMA = polydimethylsiloxane-poly(methyl methacrylate) block copolymer; initiated with $PDMS_b$-ACP initiator; $DEVP_c$-PMMA = phosphorylated PMMA initiated with $PDMS_c$-ACP initiator

[c] W_1, W_2 and W_3 are the amount of weight loss in the first, second and third step, respectively

[d] Y_c = char residue at 600°C

the d.t.a. curve; the former degradation may be due to the depolymerization of saturated end group product of disproportionation. PMMA is destroyed virtually completely at 433°C. A lower tendency to form char of PMMA in thermal degradation is related to the thermal depolymerization which yields only monomer, the monomer breaking down at higher temperature to small fragments.

PDMS-b-PMMA

The t.g.a. curve for $PDMS_c$-*b*-PMMA copolymer, with a siloxane chain length of 4100 and a siloxane content of 15.8 wt% in nitrogen atmosphere, displays three distinct regions of weight loss (*Figure 2a*) which are reflected in three peaks in the d.t.g. curve (*Figure 2b*). Above 426°C, an endothermic process[27] (426–496°C) was detected in the d.t.a. curve (*Figure 2c*). This corresponds to the third weight loss process reported previously for PDMS segments and results in depolymerization of produced volatile cyclic oligomers[28–30].

Figure 3 compares the thermal stability of PMMA with various similar PDMS-*b*-PMMA copolymers. PDMS-*b*-PMMA copolymers begin to degrade at temperature (ca. 240°C) with PMMA but degrade less precipitously as the temperature is raised. The temperature of 40% weight loss in PDMS-*b*-PMMA is increased with increasing PDMS content in copolymers (*Figure 3*). The results indicate that thermal stability of PMMA is enhanced by PDMS segments in the copolymer. Above 426°C, the PDMS segments in copolymer start to degrade. The amount of weight loss 12–21 wt% in the third step W_3 (*Table 2*) increases with increasing PDMS content in copolymer, and that is consistent to the amount 11–19 wt% calculated from ^{1}H n.m.r. (*Table 1*).

DEVP-PMMA

The t.g.a. curve for $DEVP_c$-PMMA displays two regions of weight loss (*Figure 4a*). Usually at lower heating rate the first part of the degradation curve with several peaks indicates the complexity of the degradation process. The data in *Table 2* show that the onset temperature of the first step decreases whereas char residue increases in the DEVP-PMMA copolymer, compared with the PMMA. The results may be due to the ease of thermal degradation of the phosphorus segment[10], and subsequently form anhydrides of phosphoric and related acids which may act as dehydrating agents and promote char formation[11,12]. This is apparent from the d.t.a. trace of $DEVP_c$-PMMA (*Figure 4c*) which shows one small endotherm in the region of decomposition temperature (254°C), immediately followed by an exotherm (290°C). The exothermic peak is reflected in the peak (290°C) in the d.t.g. curve (*Figure 4b*). Based on the t.g.a. traces it can be seen that phosphorylated

PMMA is thermally less stable than the corresponding PMMA, i.e. the thermal stability of PMMA is decreased with increasing content of VDEP, as shown in *Figure 5*. A similar phenomenon has been observed in certain phosphorus-containing polymers[31–33]. The weight loss of the first degraded stage increases as the phosphorus content increases, whereas that of the second degraded stage decreases (*Table 2*). Therefore, the first degraded stage is a combination of DEVP-induced and the vinyl end-induced decomposition. On the other hand, the degradation of the PDMS segments in copolymers were promoted by derivatives of DEVP.

Kinetic analysis

The apparent activation energy E_a of polymer degradation can seldom be assessed correctly from a single t.g.a. curve. A more reliable method to evaluate the E_a is isoconversional method. The method proposed by Ozawa requires several t.g.a. curves at different heating rates (B)[34]. *Figure 6* shows the relationship of the logarithm of the heating rate ($\log B$) vs. $1/T$ for each value of α (α, the degree of conversion = weight loss at a given temperature/total weight loss of the degradation) for copolymer DEVP$_c$-PMMA. From isoconversional curves, apparent activation energies are calculated from the slopes of the lines by the expression[34]

$$E_a = -\text{slope} \times R/0.457$$

where R is the gas constant. The activation energies of the samples show a large variation with degree of conversion (*Table 3* and *Figure 7*) which is expected due to the continuous change of the degradation mechanism.

PMMA

The measured activation energy (126 kJ mol^{-1}) for the first thermal degraded stage ($\alpha = 1$) of PMMA in this work is compared to the literature values caused by end initiation[24]. Moreover, the activation energies (from 143 to 200 kJ mol^{-1}) for the second thermal degraded stage ($0.2 < \alpha < 0.9$) increase with increase in conversion, as shown in *Figure 7*. Since the values of activation energies for PMMA degradation initiated by random scission are 207[35], 210[36] and 233 kJ mol^{-1} (ref. 37), thus a competition takes place between end initiation and random scission initiation at second weight loss stage.

PDMS-PMMA

The trend of activation energy for PDMS-PMMA copolymer is similar to the PMMA, increasing with conversion (*Figure 7*). However, the activation energy for the initiation, E_a ($\alpha = 0.1$), is higher than that of PMMA. The result indicates that the thermal stability of PMMA is enhanced by PDMS. After 40 wt% weight loss, the activation energy of degradation in PDMS-*b*-PMMA is slightly greater than that in PMMA. Furthermore, the apparent activation energies of degradation are dropped at high conversion ($0.8 < \alpha < 0.9$), which corresponds to the degradation of PDMS. The low activation energies are approximately consistent with the literature (177 kJ mol^{-1})[38] initiated from a cyclic four-centred transition state accompanied by siloxane bond rearrangement.

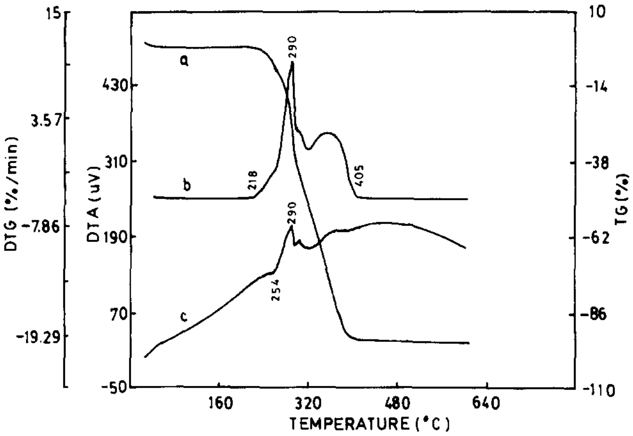

Figure 4 T.g.a. (a), d.t.g. (b), and d.t.a. (c) curves of sample DEVP$_c$-PMMA at the heating rate 10°C min^{-1} under nitrogen atmosphere

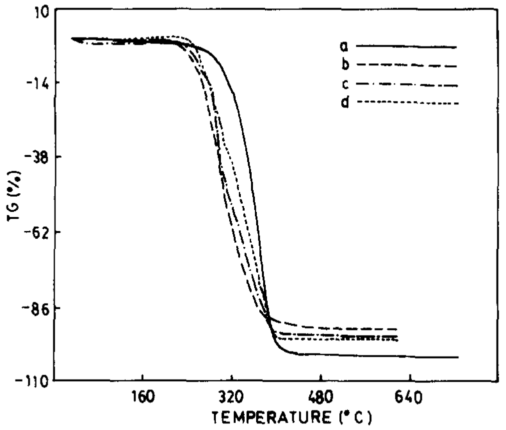

Figure 5 T.g.a. curves of sample DEVP-PMMA at the heating rate 10°C min^{-1} under nitrogen atmosphere: (a) PMMA, (b) DEVP$_b$-PMMA, (c) DEVP$_c$-PMMA, and (d) DEVP$_e$-PMMA

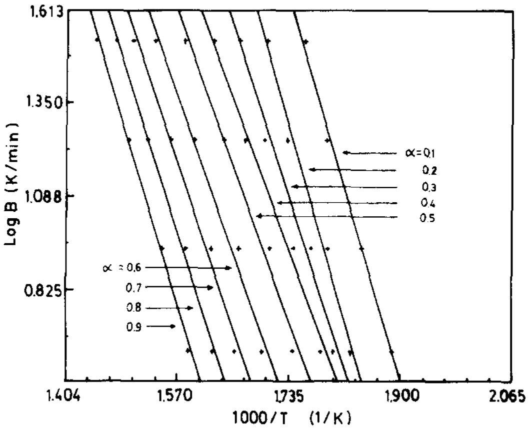

Figure 6 The dependence of logarithm of heating rate ($\log B$) vs. reciprocal absolute temperature ($1/T$) for the Ozawa method at indicated conversions (α) of decomposition of DEVP$_c$-PMMA in nitrogen

DEVP-PMMA

The activation energy of thermal degradation for the phosphorylated PMMA is lower than that for unmodified PMMA, as shown in *Figure 7*. E_a is decreased with increasing conversion in $0.1 < \alpha < 0.4$, whereas it increases with increasing conversion in $0.5 < \alpha < 0.9$. It indicates that the DEVP-PMMA copolymers with

Table 3 Activation energies (E_a) in kJ mol^{-1} of the PMMA degradation process calculated by the Ozawa method[a]

Polymer[b]	Conversion (α)[c] 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
PMMA	126	143	161	173	186	191	196	200	195
$PDMS_b$-*b*-PMMA	185	132	154	173	205	223	237	241	217
$PDMS_c$-*b*-PMMA	136	143	162	173	188	199	207	210	127
$PDMS_e$-*b*-PMMA	155	132	143	161	179	198	218	164	128
$DEVP_b$-PMMA	119	109	99	87	88	88	86	96	116
$DEVP_c$-PMMA	118	121	106	93	96	97	103	108	114
$DEVP_e$-PMMA	124	114	101	94	92	97	104	112	115

[a] $E_a = -\text{slope} \times R/0.457$

[b] $PDMS_b$-*b*-PMMA = polydimethylsiloxane-poly(methyl methacrylate) block copolymer; initiated with $PDMS_b$-ACP initiator; $DEVP_c$-PMMA = phosphorylated PMMA initiated with $PDMS_c$-ACP initiator;

[c] Conversion = $1 - (W/W_0)$, where W_0 and W represent initial weight and weight at any time

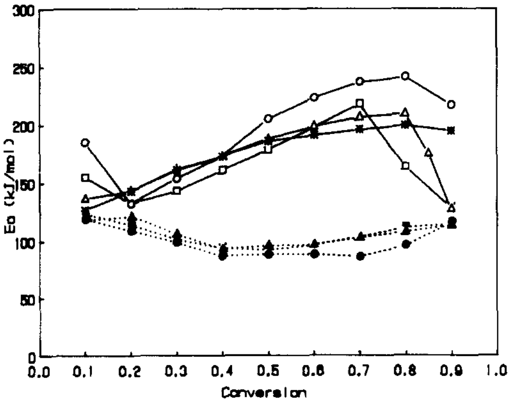

Figure 7 The dependence of E_a calculated by the Ozawa method on the degree of conversion α for polymers: $*$, PMMA; ○, $PDMS_b$-*b*-PMMA; △, $PDMS_c$-*b*-PMMA; □, $PDMS_e$-*b*-PMMA; ●, $DEVP_b$-PMMA; ▲, $DEVP_c$-PMMA; ■, $DEVP_e$-PMMA

phosphorus backbone have a promoting effect on chain scission[10]. Moreover, the average activation energy $E_{a,av}$ ($0.1 < \alpha < 0.9$) is decreased (from 107 to 99 kJ mol^{-1}) with increasing phosphorus content in phosphorylated PMMA (from 0.9 to 1.6 wt%). The low activation energy is probably due to presence of P–O–C bonds which are susceptible to chain scission during thermal degradation and act as weak links[39,40].

CONCLUSIONS

The polymers with silicon and phosphorus were subjected to t.g.a. in nitrogen. The trends in thermal behaviour and apparent activation energies of degradation with change in composition were examined and compared with that of the unmodified PMMA. The incorporation of PDMS segments in block polymers improved thermal stability of PMMA. The silicon functionalization affected the initial ($\alpha = 0.1$) thermal degradation of PMMA segments in PDMS-*b*-PMMA copolymers with higher activation energies than that of PMMA. However, phosphorylated PMMA caused an easy thermal degradation and lower activation energy of degradation. The average activation energy (99–107 kJ mol^{-1}) of thermal degradation ($0.1 < \alpha < 0.9$) for the phosphorylated PMMA was found to decrease with increase in phosphorus content (from 0.9 to 1.6 wt%).

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