

A Thermal Analysis Study of Bisphenol-A-Polycarbonate-Dimethylsiloxane Block Copolymers

GARY R. GRUBBS and MARY E. KLEPPICK, *Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261* and J. H. MAGILL, *Department of Metallurgical and Materials Engineering and Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261*

Synopsis

The thermogravimetric analysis (TGA) of three block copolymers of poly(dimethylsiloxane)-Bisphenol-A-polycarbonate was measured in nitrogen and air from just above room temperature to 1000 K. Measurements were made on a Perkin-Elmer TGS-2 system equipped with a System 4 microprocessor controller. Weight loss curves were obtained for heating rates ranging from 1.5 (or lower) to 80°C/min. Results were analyzed according to the method of Flynn and Wall. Two degradation reactions were observed in air and in nitrogen, respectively. In air, the activation energy was found to be 28–35 kcal/mol. In the inert atmosphere, activation energies were 44 ± 3 kcal/mol and 11–27 kcal/mol, respectively. No straightforward relationship was found between the thermal stability of the copolymers and their composition. The morphology of char residues formed at 80°C/min heating rate to 1000 K have been examined in relation to the Si content. The degree of char formation at different heating rates has been established in nitrogen and in air, respectively.

INTRODUCTION

Silicone polymers have thermal stabilities superior to many organic materials.¹⁻⁹ In combination with aromatic structures, such as polycarbonates, which also possess good thermal properties, the final product may possess some of the best qualities of both polymeric ingredients.^{1,2,7,8,10} This is especially true when both constituents are present in block form² and of variable or fixed length(s). Block copolymers¹ are now well recognized as high performance thermoplastics that possess desirable qualities such as good (1) impact strength, (2) toughness, (3) flame resistance, (4) flexibility, (5) thermal stability, and other properties depending upon their composition and structure. Tailor-made qualities^{1,11,12} may be incorporated in macromolecules through the judicious choice of substituents and synthetic procedures. Optimum physical properties^{1,2,13,14} can be arrived at via the proper choice of chain backbone or substituents, degree of polymerization, and block dimensions commensurate with commercial and/or other requirements. Based upon experience or material evaluation procedures, the most apt characteristics compatible with cost or other constraints may be incorporated into the required polymer.

Since this paper is primarily concerned with kinetic aspect of thermal stability in inert and oxidative environments, it is appropriate to review briefly the literature information on bisphenol-A-polycarbonate (BPAC)¹⁵⁻¹⁸ and poly(dimethylsiloxane) (PDMS). In summary, BPAC exhibits thermal decomposition

below 250°C. Above 250°C, the degradation begins with reactions at the end groups. These are primarily oxidative reactions.¹⁶ Below 400°C, the carbonate group is degraded, while above 400°C depolymerization reactions such as chain scission and condensation compete in the decomposition processes. Chain scission is the predominant reaction whenever degradation products remain in the system, whereas, if such products are removed, condensation reactions dominates.¹⁶ At temperatures in excess of 500°C, a more complex situation exists. Many reactions, such as chain scission, hydrolysis, crosslinking, and decarboxylation may compete in the thermal degradation of the polymer.

PDMS is stable below 320°C. It has been reported²⁻⁴ to degrade in a two-step process between 320°C and 400°C. A thermooxidative reaction first occurs, oxidizing the methyl groups. Above 400°C, a randomly initiated depolymerization reaction takes place, giving rise to cyclic dimethylsiloxanes and low-molecular-weight linear residues. To some extent, cyclization reactions may be reduced through strengthening the Si—O bond by attaching electron withdrawing groups to the silicon.^{7,8} In this regard, phenyl type or carborane groups have proved to be effective. This modification either raises the threshold temperature for degradation or changes the mechanism for the formation of cyclic oligomers, thus promoting some degree of crosslinking and preventing ring formation and char formation at high temperatures. So far, these two processes have not been identified and distinguished in the literature, although either homopolymer BPAC or DMS is relatively stable, but impurities will catalyze and/or impair their resistance to thermal stress. In practice, additives are usually employed industrially to combat degradation and discoloration.

To some extent, the development of copolymers of BPAC/DMS (used in the present investigation) have benefited from recent advances in polymer technology providing silicone-containing alternating block copolymers that have been designed to meet specific needs.^{1,12,19} The purpose of this paper is to evaluate some of the thermal properties of a selected group of three block copolymers containing dimethylsiloxane block dimension which seems adequate to enhance many of the physical properties of the bisphenol-A-polycarbonate, which is the other copolymer constituent. Although each polymer has many characteristics, it is very difficult to optimize on all aspects of physical properties, as a recent report has indicated.¹ Still, major commercial goals can be met in order to satisfy stringent demands, particularly in regard to mechanical properties and flammability criteria. For instance, Limiting Oxygen Index values approaching 50 have been found for some BPAC/DMS materials.¹ Furthermore, a correlation has been reported between residues formed at 700°C approximately and the SiO₂ level in the copolymer, but other complex reactions involving carbon are also contributory to residue formation.

It has been suggested that the incorporation of polysiloxane components in a copolymer impart flame-retardant qualities without halogens, the latter frequently introducing toxicological problems^{20,21} when polymers undergo thermooxidative reactions. So far, not enough attention has been given to this problem, which is of considerable importance whenever the polymer encounters thermally hostile environments. Some evaluation of the thermal degradative behavior in BPAC/DMS copolymer is presented in this paper.

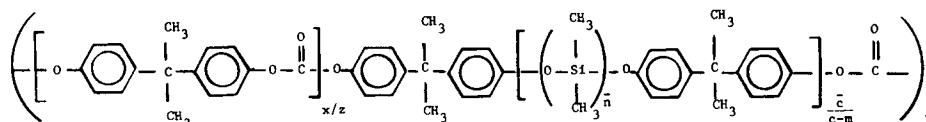


Fig. 1. Physical structure of the poly(dimethylsiloxane)/bisphenol-A-polycarbonate block copolymer. (See Ref. 28.)

EXPERIMENTAL

Materials

Copolymers of bisphenol-A-polycarbonate (BPAC) and dimethylsiloxane (DMS) with a DMS block size of approximately 20 units were kindly provided by Dr. Roger Kambour of the General Electric Co., Schnectady, New York. The chemical structure of the copolymer is illustrated in Figure 1, and the three sample compositions are listed in Table I; they are free of additives except for remnants of catalyst residues which are sometimes difficult to remove entirely.

Measurements

Thermal Analysis

Thermal stability measurements were made in air and in nitrogen. A Perkin-Elmer TGS-2 instrument with a System 4 microprocessor controller was used to perform the thermogravimetric analysis (TGA). Heating rates used in this investigation ranged mostly from 1.5 to 80°C/min. Sometimes rates as low as 0.6°C/min were used. In all instances, gas flow rates were 25 mL/min. The sample size was 3–4 mg, approximately, for a given run. At least duplicate measurements were made at each specified heating rate.

The char yield in any run was determined from the appropriate thermogram.

SEM/EDAX Analysis

The chars formed upon heating specimens at 80°C/min to 750°C in nitrogen and in air were examined in a scanning electron microscope, type AMR/200 fitted with energy dispersive analysis (EDAX) accessories. The morphological features

TABLE I
Composition of the PDMS—PBAC Block Copolymer Samples^a

Sample no.	Wt % DMS ^b	Wt % PBAC ^b	Average DMS block length
I	65 (62.8)	35 (37.2)	20
II	25 (21.9)	75 (78.1)	20
III	50 (47.8)	50 (52.2)	20

^a Materials were kindly provided by Dr. Roger Kambour, General Electric Co., Schnectady, N.Y.

^b Later characterization of these samples²⁶ indicates that the values in parentheses are more accurate. The rounded numbers are retained here to facilitate comparison with earlier literature.

of these chars as well as their Si content was assessed by energy dispersive X-ray analysis (EDAX). Quantitative analysis of Si content in char residues was determined analytically by Galbraith Laboratories, Inc., Knoxville, TN.

Kinetic Analysis

Using the analytical approach of Flynn and Wall²² activation energies E of polymer degradation were determined from the non-TGA runs. They were derived by making crossplots of the logarithm of the heating rate β ($= dT/dt$) vs. the reciprocal of the absolute temperature T at a selected degree of conversion C , which must not be too large. In these circumstances at constant conversion rate dC/dt ,

$$\frac{dC}{dT} = \frac{A}{\beta} f(C) \exp(-E/RT)$$

where E is expressed as $-4.35 d \log \beta/d(T^{-1})$. In this equation, A is a preexponential factor (constant) and R is the gas constant.

RESULTS AND DISCUSSION

(Thermograms were generated for each run for the three block copolymer samples investigated. Six and often seven different heating rates from room temperature up to 750°C were used in air and in nitrogen.) Representative thermograms, weight loss and first derivative curves, for the three copolymer samples at a heating rate of 1.5°C/min in both air and nitrogen respectively are shown in Figures 2, 3, and 4. Degradation curves at the other heating rates in similar environments are presented in Figures 5, 6, and 7. These curves indicate

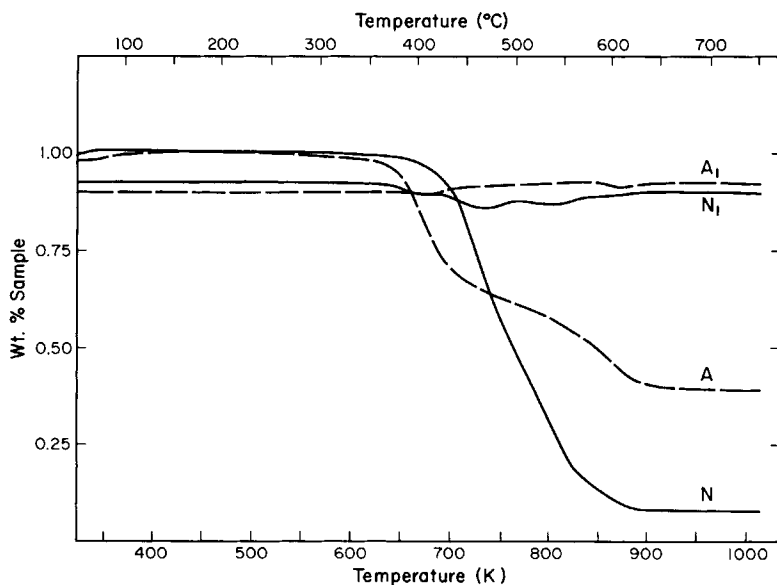


Fig. 2. Thermogram for the block copolymer sample I, containing 65 wt % DMS (block size 20 units) and 35 wt % PBAC with a heating rate of 1.5°C/min. Curves N and A are weight loss curves in nitrogen and air, respectively, and N_1 and A_1 are the corresponding first derivative curves.

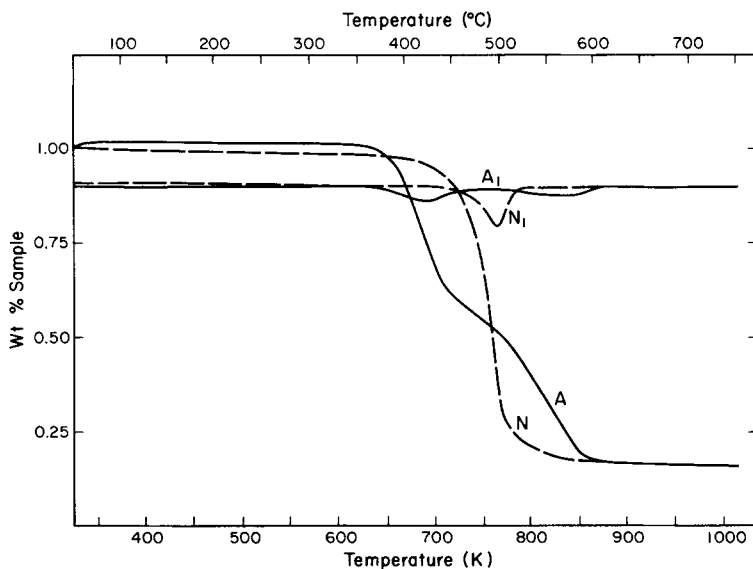


Fig. 3. Thermogram for the block copolymer sample II, containing 25 wt % DMS (block size 20 units) and 75 wt % PBAC with a heating rate of 1.5°C/min. Curves N and A are weight loss curves in nitrogen and air, respectively, and N₁ and A₁ are the corresponding first derivative curves.

that two degradation reactions are present. The temperature ranges for the initial decomposition temperature (IDT) corresponding to the onset of 2.5% weight loss in the two different environments are presented in Table II for comparison. The thermal stability of the samples at selected heating rates in air and in nitrogen are summarized in Tables III and IV. Values are expressed in terms of wt % of starting material.

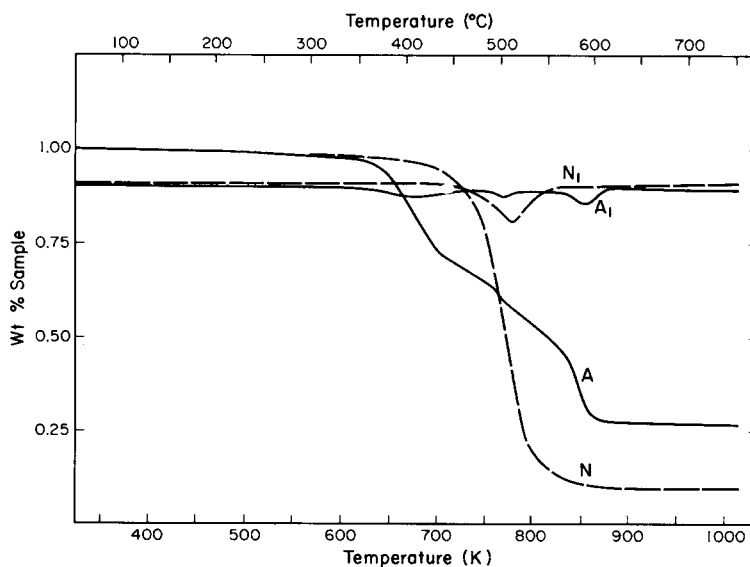


Fig. 4. Thermogram for the block copolymer sample III, containing 50 wt % DMS (block size 20 units) and 50 wt % PBAC with a heating rate of 1.5°C/min. Curves N and A are weight loss curves in nitrogen and air, respectively, N₁ and A₁ are the corresponding first derivative curves.

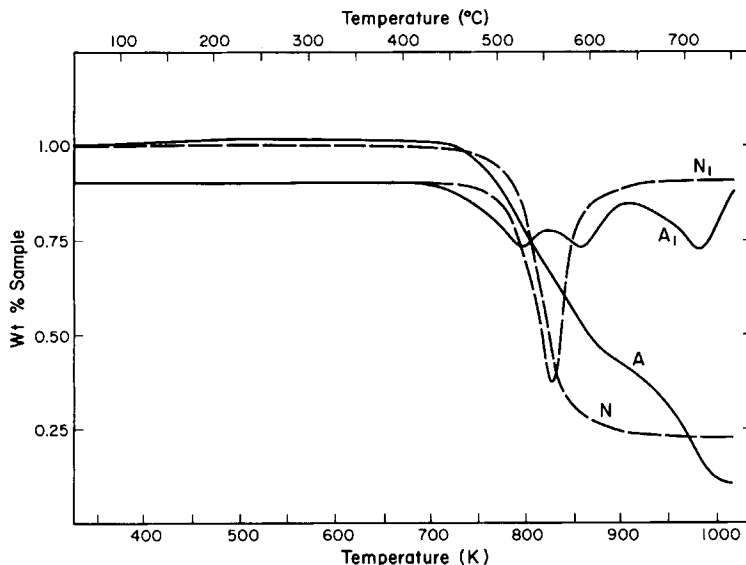


Fig. 5. Thermogram for block copolymer sample II, containing 25 wt % DMS (block size 20 units) and 75 wt % PBAC with a heating rate of 20°C/min. Curves N and A are weight loss curves in nitrogen and air, respectively, and N_1 and A_1 are the corresponding first derivative curves.

Plots of $\log \beta$ vs. $1/T(K)$, at constant conversion are shown in Figures 8–13. From these graphs, values of the activation energy(s) for thermal degradation were calculated by the method outlined by Flynn and Wall²² and are tabulated in Table V. In Table VI, values of the activation energy for the homopolymers, polydimethylsiloxane, and bisphenol-A-polycarbonate, determined by other investigators, are shown for comparison with our results.

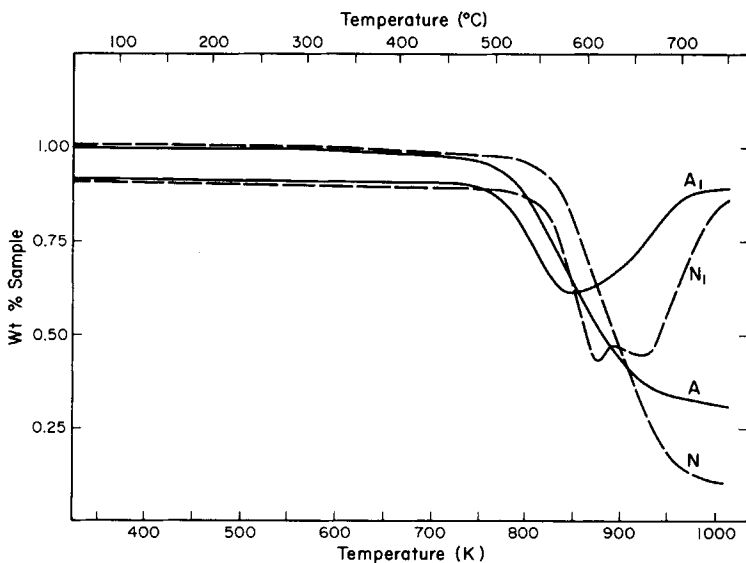


Fig. 6. Thermogram for the block copolymer sample I, containing 65 wt % DMS (block size 20 units) and 35 wt % PBAC with a heating rate of 80°C/min. Curves N and A are weight loss curves in nitrogen and air, respectively, and N_1 and A_1 are the corresponding first derivative curves.

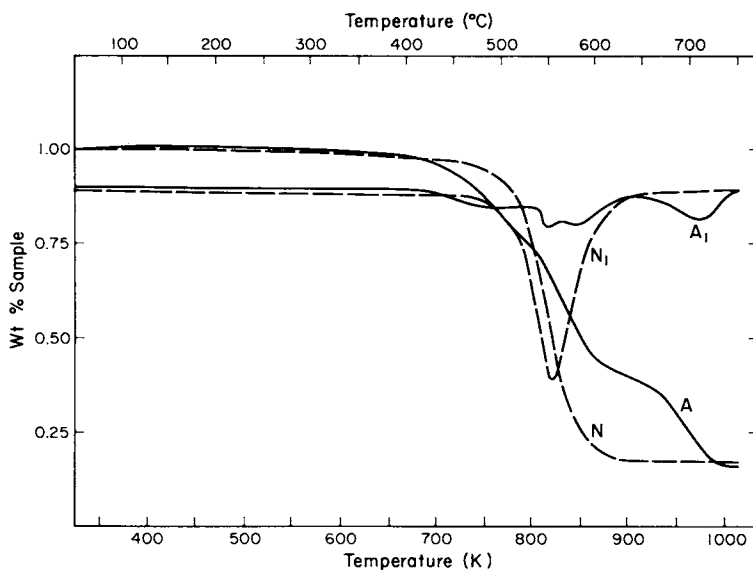


Fig. 7. Thermogram for the block copolymer for sample III, containing 50 wt % DMS (block size 20 units) and 50 wt % PBAC with a heating rate of 10°C/min. Curves N and A are weight loss curves in nitrogen and air, respectively, and N_1 and A_1 are the corresponding first derivative curves.

In air, the activation energies for our copolymers ranged from $28.2 \pm .4$ kcal/mol to 35.6 ± 3.5 kcal/mol for the initial or first degradative reaction E_1 . This value compares well with results reported by other investigators. For instance, Thomas and Kendrick⁴ presented an initial activation energy of 30 kcal/mol for PDMS in air, Lee¹⁸ cited a value for the activation energy for BPAC of 33 kcal/

TABLE II
Initial Decomposition Temperatures (IDT)^a

Sample no.	Wt % DMS	IDT (°K)	Environment
II	25	657-787	air
III	50	613-719	air
I	65	637-735	air
II	25	680-794	N ₂
III	50	663-745	N ₂
I	65	688-810	N ₂

^a Initial decomposition temperatures occurred at conversion, $C = 2.5\%$.

TABLE III
Thermal Stability of DMS—PBAC Copolymers in Air at Selected Heating Rates

	Sample no.	% sample				
		350°C	400°C	450°C	500°C	550°C
Heating rate 1.5°C/min	I	98	85	66	62	56
	II	100	90	61	51	41
	III	97	87	70	60	50
Heating rate 20°C/min	I	99.5	98	92.5	74	62
	II	100	100	100	88	67
	III	99.5	98	94	80	52

TABLE IV
 Thermal Stability of DMS—BPAC Copolymers in N₂ at Selected Heating Rates

	Sample	% sample				
		350°C	400°C	450°C	500°C	550°C
Heating rate 1.5°C/min	I	100	98	82	31	20
	II	98	97	90	35	17
	III	97	96	91	68	14
Heating rate 20°C/min	I	99	98	97.5	95	83
	II	100	100	99	98	60
	III	98	97.5	96	94	55

mol, and Knight¹⁰ quoted values of 29.4 kcal/mol for BPAC and 14.1 kcal/mol for PDMS, respectively. The latter value has been attributed³ to a high-temperature-catalyzed reaction. In general, it has been shown that replacing one of the methyl groups in PDMS lowers its activation energy. Where ethyl or propyl substituents are used, the value drops to 30 kcal/mol and 23 kcal/mol, respectively. However, a phenyl substituent raises it once more to 40 kcal/mol.

The Flynn–Wall model used for kinetic analysis is most reliable at lower degrees of conversions. This limitation prevents an accurate evaluation of the activation energy for a second reaction, particularly for our copolymer samples that are degraded in air, since two reactions occur in all PDMS—PBAC copolymers examined. The first reaction seen to occur in the lower temperature regime, illustrated in Figures 8, 9, and 10, is believed to be a thermooxidative reaction wherein the methyl groups of the dimethylsiloxane portion of the macromolecules and the end groups of the polycarbonate portion are involved. A second reaction, occurring at higher temperatures, for which no activation energy was determined, is most likely to be a depolymerization process wherein the chain backbone of the copolymer is attacked at the siloxane bond and/or the carboxyl group.

Recently, detailed investigations^{7,8} have demonstrated that electron withdrawing groups attached to silicon can strengthen Si—O bonds through enhancing the interaction of the oxygen lone pair electrons in bonding, thus reducing the propensity for cyclization reactions, as phenyl substituents have shown. Moreover, in poly(dodecacarborane–silanes), the percent weight measured in argon at 800°C is reduced because the *m*-carborane impedes the chain depolymerization compared to poly(DMS) itself. Here²³ it has been pointed out that phenyl-substituted carboranes impart additional thermal stability in

 TABLE V
 Activation Energies of Polymer Samples

Sample no.	Wt % DMS	Activation energy (kcal/mol)			Environment
		E_1	E_2	E_3	
I	65	32.7 ± 0.8	—	—	air
II	25	28.2 ± 0.4	—	—	air
III	50	35.6 ± 3.5	—	—	air
I	65	—	41.4 ± 3.7	11.2 ± 1.3	N ₂
II	25	—	43.3 ± 3.2	26.9 ± 6.0	N ₂
III	50	—	47.0 ± 2.7	24.8 ± 3.5	N ₂

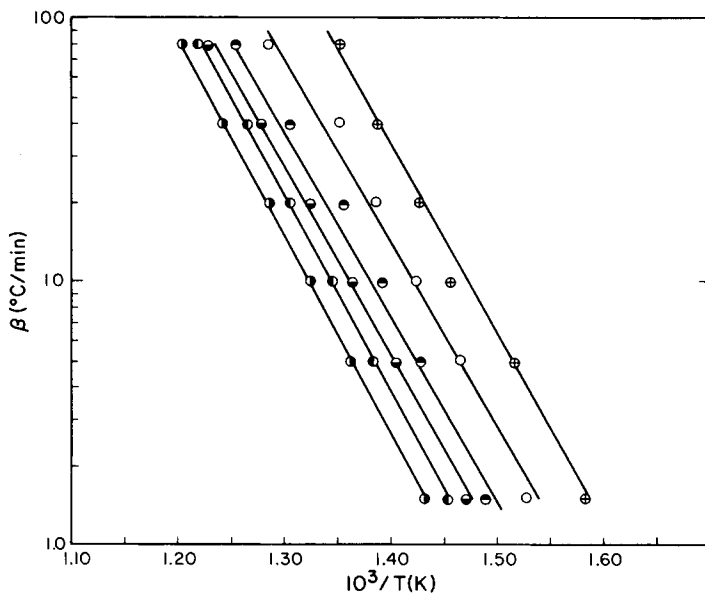


Fig. 8. Plot of $\log \beta$ vs. $10^3/T$ for sample I, containing 65 wt % DMS (block size 20 units) and 35 wt % PBAC, in air. Conversion (%): (⊕) 2.5; (○) 5; (●) 10; (◐) 15; (◑) 20; (◒) 25.

accordance with the fact that such groups promote crosslinking and, consequently, reducing sample weight loss. On the other hand, relatively short DMS side groups attached to polycarbonate only improved marginally the thermal behavior of this polymer compared with the original homopolymer. The fact that the activation energies for PDMS and PBAC homopolymers are not very different (see Table VI) poses a real problem which cannot be resolved without

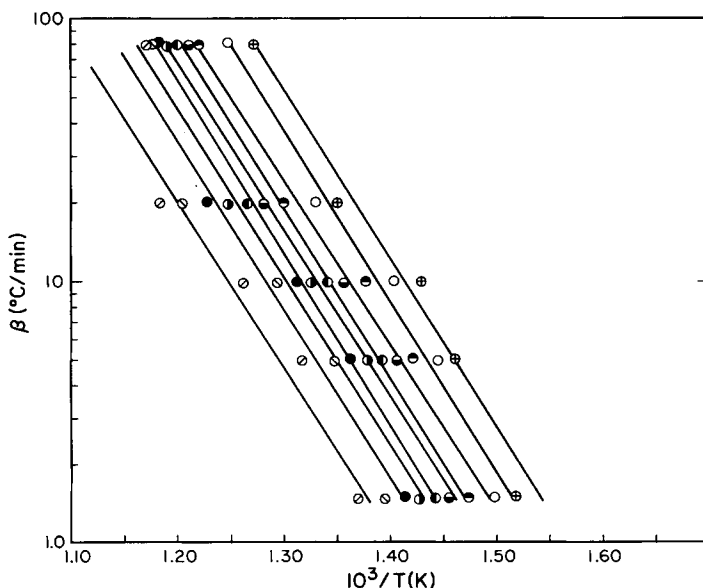


Fig. 9. Plot of $\log \beta$ vs. $10^3/T$ for sample III, containing 25 wt % DMS (block size 20 units) and 75 wt % PBAC, in air. Conversion (%): (⊕) 2.5; (○) 5; (●) 10; (◐) 15; (◑) 20; (◒) 25; (◓) 30; (◔) 35; (◕) 40.

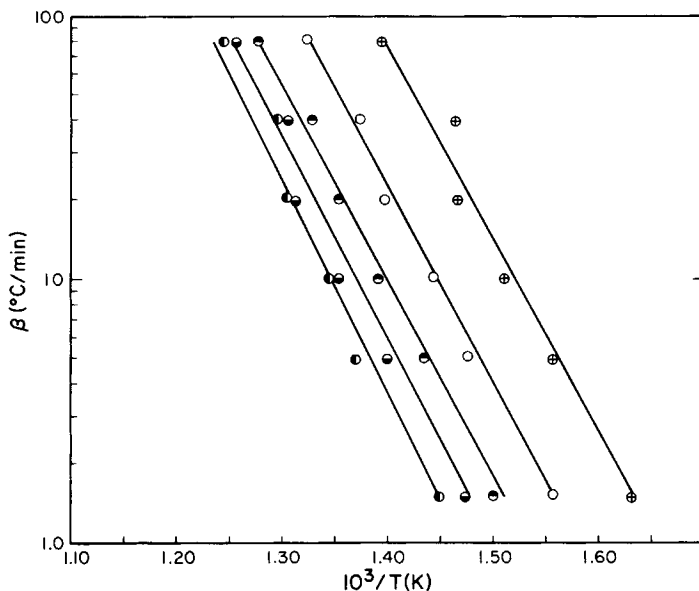


Fig. 10. Plot of $\log \beta$ vs. $10^3/T$ for sample III, containing 50 wt % DMS (block size 20 units) and 50 wt % BPAC, in air. Conversion (%): (○) 2.5; (○) 5; (●) 10; (●) 15; (●) 20.

recourse to a detailed GC/mass spectrometer analysis and concomitant molecular weight (GLC) analysis of the solid phase residue that arises.

However, from the experimental thermograms in nitrogen, two reactions are indicated. The second activation energy is apparent in Figures 11–13; the lower activation energy found here may be indicative of a catalyzed reaction similar to that suggested by Kucera and Lanikova.²¹ Although it has been demonstrated that only C—H²⁴ and Si—C²⁵ bonds are ruptured when PDMS and polymethyl

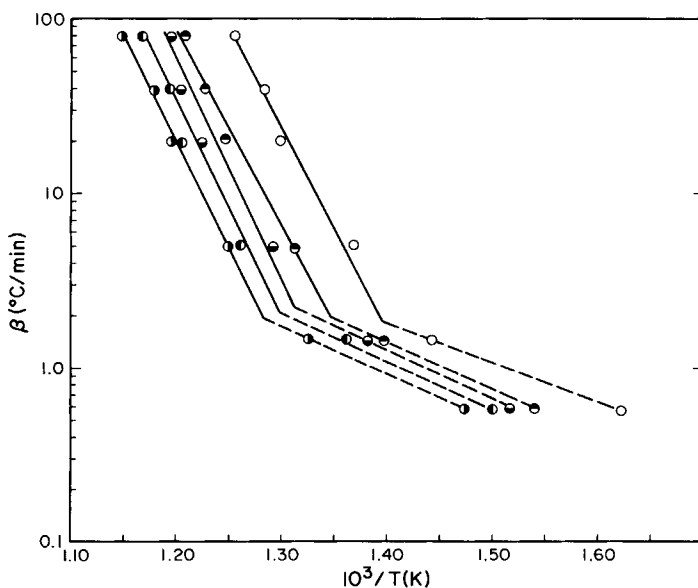


Fig. 11. Plot of $\log \beta$ vs. $10^3/T$ for sample I, containing 65 wt % DMS (block size 20 units) and 35 wt % BPAC, in nitrogen. Conversion (%): (○) 5; (●) 10; (●) 15; (●) 20; (●) 25.

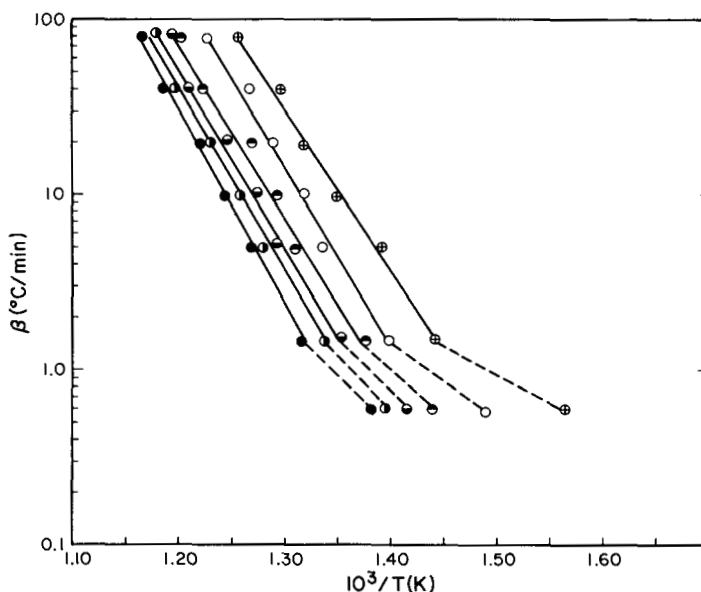


Fig. 12. Plot of $\log \beta$ vs. $10^3/T$ for sample II, containing 25 wt % DMS (block size 20 units) and 75 wt % BPAC in nitrogen. Conversion (%): (○) 2.5; (○) 5; (○) 10; (○) 15; (○) 25; (●) 30.

phenylsiloxanes are degraded by UV light, heterocyclic cleavage of Si—O will occur in the presence of electrophilic and nucleophilic reagents (including impurities). The reaction associated with the higher activation energy in PDMS has been attributed¹ to the formation of a transition-state complex followed by Si—O bond scission as suggested by Thomas et al.⁴ and others. In an extensive treatise on siloxanes from the Russian literature,²⁶ it has been claimed that the cleavage of Si—O—Si occurs via a molecular transfer mechanism, thus ac-

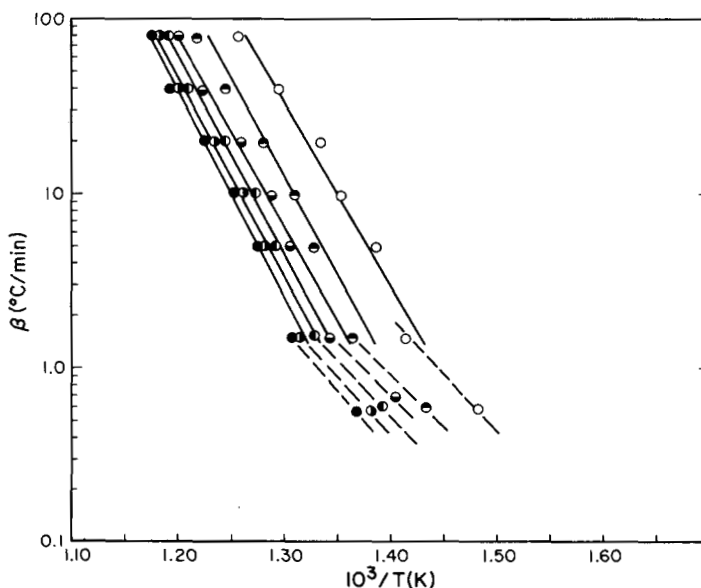


Fig. 13. Plot of $\log \beta$ vs. $10^3/T$ for sample III, containing 50 wt % DMS (block size 20 units) and 50 wt % BPAC in nitrogen. Conversion (%): (○) 5; (○) 10; (○) 15; (○) 20; (○) 25; (●) 30.

TABLE VI
Literature Values of Activation Energy for DMS-Type Polymers

Material	E_1 (kcal/mol)	E_2 (kcal/mol)	Environment	Reference source
Poly(dimethylsiloxane)	44.5	17.1	N ₂	2
	30	43 ± 3	air	3
	14.1	32	air	9
Poly(tetramethyl-P-silphenylene) siloxane/ polydimethyl siloxane	42.7	14.1	N ₂	2
Bisphenol-A polycarbonate ^a	36.5	—	air	16
	33	55	air	18
	29.4	41.3	air	9
Poly(tetramethyl-P-silphenylene) siloxane	44.3	14.2	N ₂	2

^a Note that degradation values in nitrogen are not available.

counting for the low activation energy (20–70 kcal/mol) for thermal degradation, compared to the calculated Si—O bond energy from the heat of combustion (101–120 kcal/mol).

Char Formation

The char level was determined for each copolymer as a function of heating rate and environmental conditions. Generally, the residues formed in nitrogen appear dark, whereas those formed in an oxidative environment also consist of relatively large amounts of greyish material (oxides of silicon). Figure 14 simply illustrates how the limiting char level corresponding to the upper flat region of the TGA curve depends upon heating rate from 0.6 to 80°C/min. Two trends in the char level are evident depending upon the environmental conditions of degradation. Heating in air, Figure 14 for instance, leads to a reduction in char residue where the weight losses recorded are in order I > III > II as the asymptotic

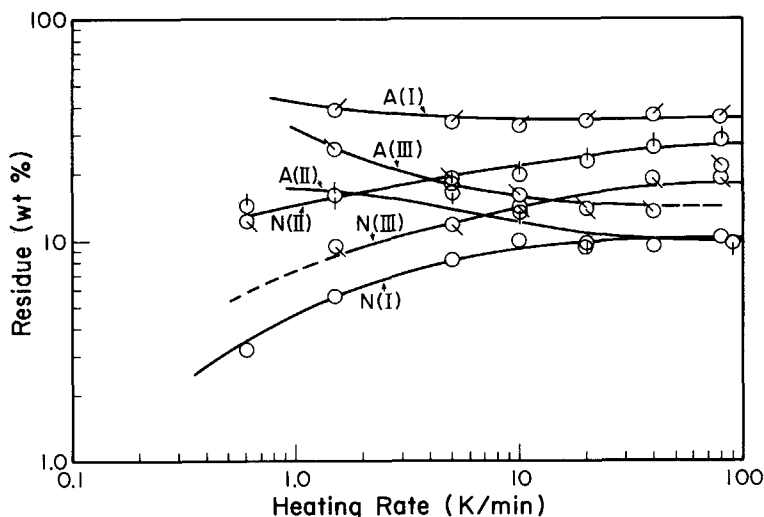


Fig. 14. Char residue (wt %) vs. heating rate (°K/min) for samples I, II, and III pyrolyzed in air, A, and in nitrogen, N, respectively, at 80°C/min, heating rate.

limit is approached at higher rates and temperatures. By way of contrast in a nonoxidative nitrogen atmosphere, a different trend is observed where levels lie in order II > III > I. With the exception of sample II with the lowest DMS wt %, the char production in air is usually larger than it is in nitrogen. Only the Si content of the char residues of these copolymers has been examined here, even though it is realized that the structure of the chars *per se* holds the clue to the innate fire retardant qualities of the copolymers in question.¹ In this article, it has been shown that there is a strong correlation between Si content and LOI index in general. However, the volatile products of degradation cannot be ignored since they are generally related, *inter alia*, with the toxicity of the volatile products of degradation. In this work, however, only the silicone content of the residues for the highest heating rate used in air and in nitrogen was determined using an EDAX analyzer attached to the scanning electron microscope, which also provided the micrographs referred to later. (This rapid heating rate was used to simulate more closely the practical conditions experienced by samples under high heat fluxes.) The analytical results in Figures 15 and 16 contain

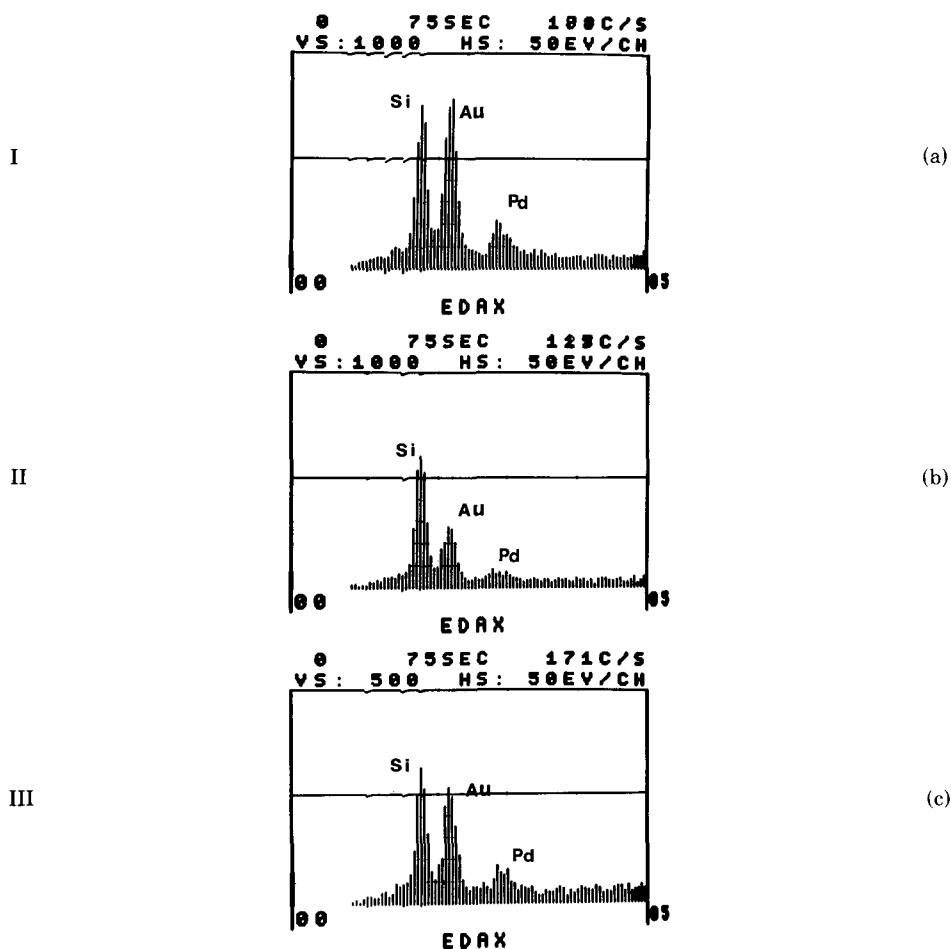


Fig. 15. EDAX signal (in SEM) from pyrolyzed samples I-III of copolymers in nitrogen. Residues were prepared by heating at 80°C/min to 750°C. Spectral lines are Si (K), Au (M), and Pd (L). Full scale is variable among samples for 75-s counting period.

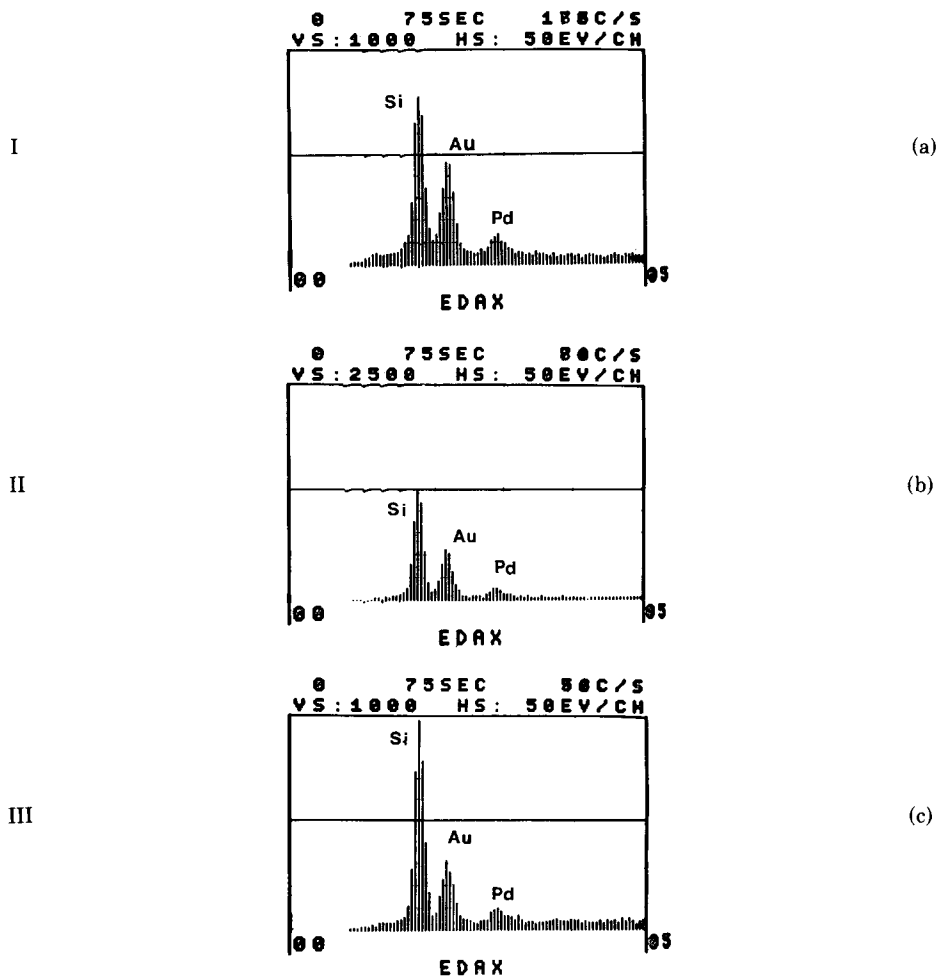


Fig. 16. EDAX signal in SEM from copolymers I-III. Residues obtained by heating in air to 750°C at 80°C/min. Spectral lines are Si (K), Au (M), and Pd (L). Full scale variable among samples for 75-s counting period.

spectral lines for Si (K) at 1.74 eV, Au (M) at 2.2 eV and Pd (L) at 2.9 eV. The Au and Pd comes from the coating material. The peak heights of Si relative to Au or Pd are evaluated later in regard to the Si or DMS content of the undegraded polymers.

The corresponding char morphologies of the DMS/BPAC copolymers, degraded in nitrogen and air, are shown in Figures 17 and 18, respectively. Variations in morphology are noted in Figure 19.

Morphology and Analysis of Chars

The chemistry and weight percent of each polymeric component of the copolymer, as well as the environmental circumstances whereby the original sample is converted into char is significant. Although temperature gradients within samples are comparatively small in TGA work, nevertheless, thermal stresses

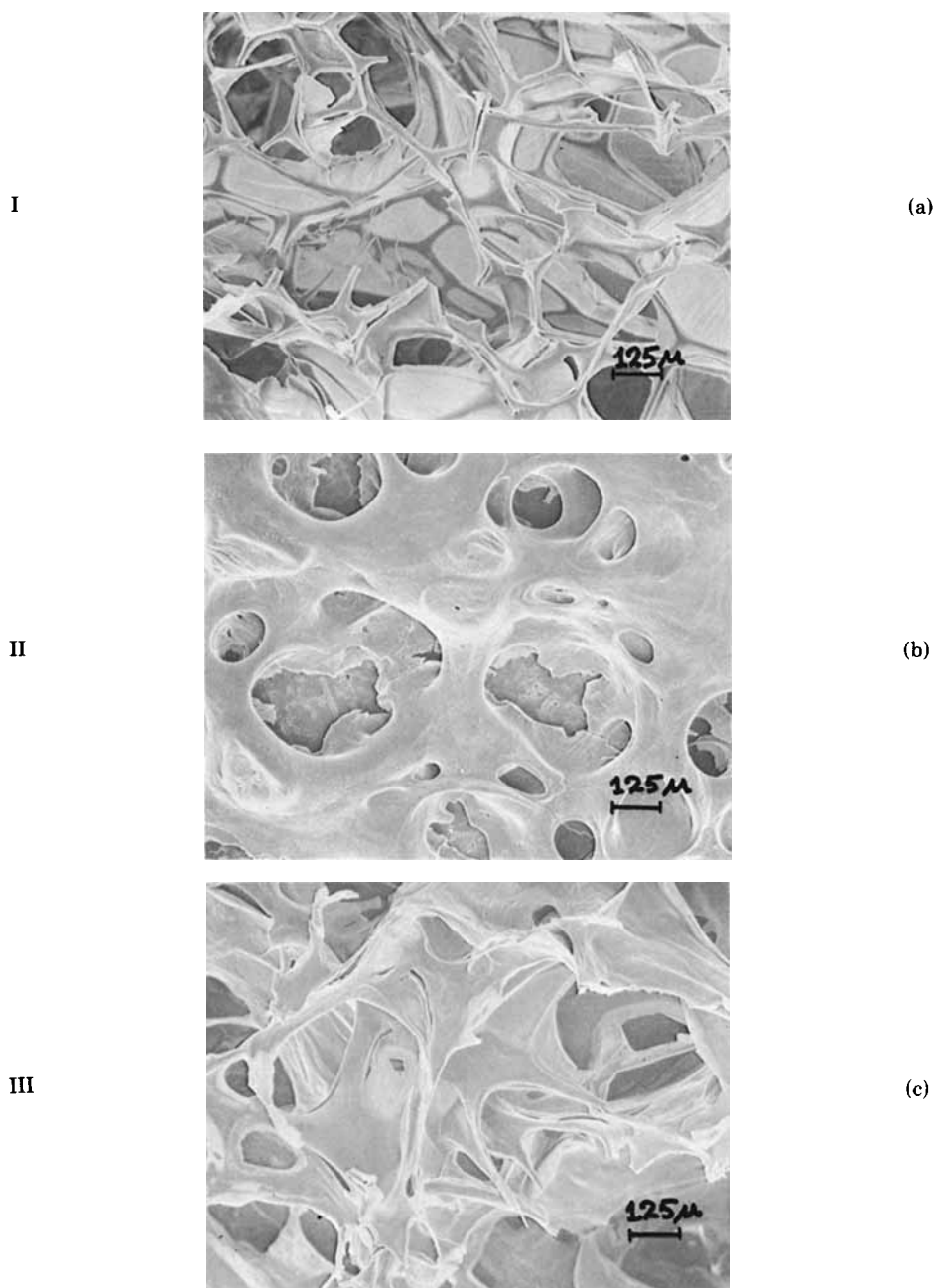
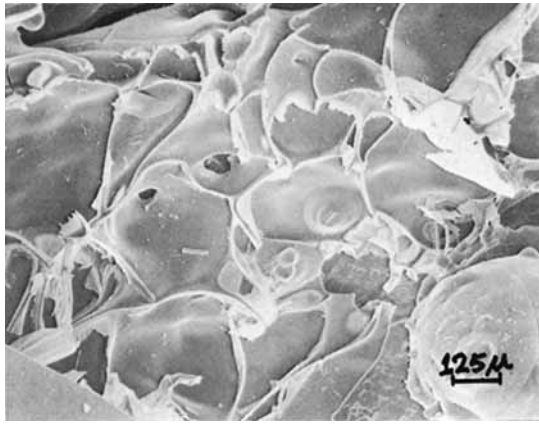


Fig. 17. Morphology of char residues of copolymers made by heating at $80^{\circ}\text{C}/\text{min}$ in nitrogen. Scanning electron micrographs were prepared using gold-palladium-coated samples.

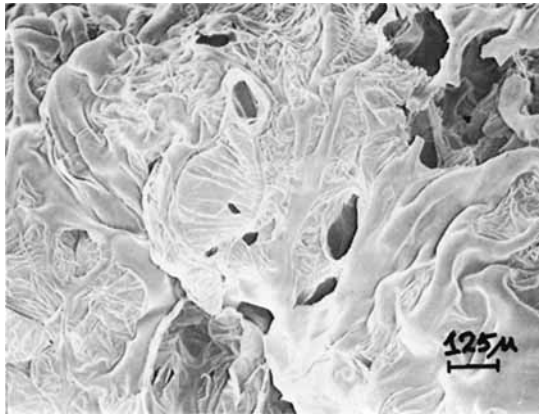
exist so that the texture or morphology of the residue reflects to some degree the thermal decomposition conditions wherein gas and bubble evolution occurs. For identical heating rates, the thermal decomposition profiles (Figs. 2-7) differ because the ratio of DMS/BPAC appears to influence char textures through the degradation kinetics. For instance, Figure 17(a)-(c) shows that when decom-

I



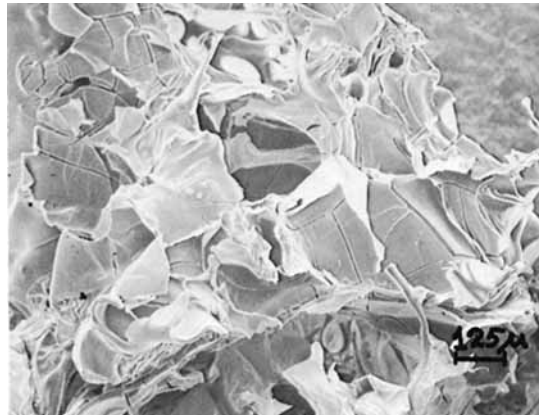
(a)

II



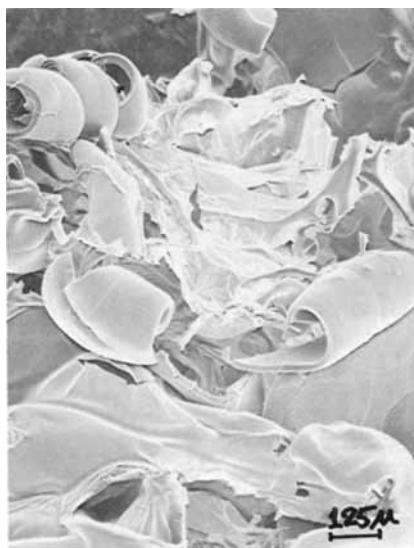
(b)

III

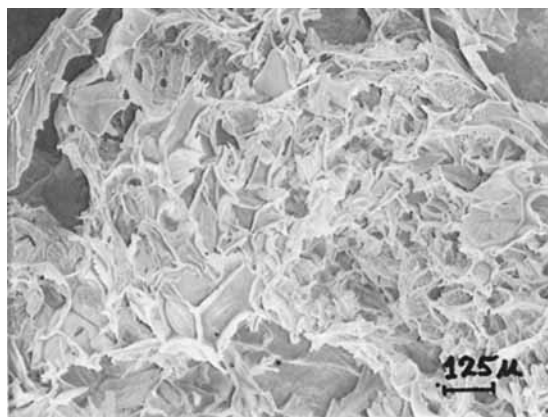


(c)

Fig. 18. Morphology of char residues of copolymers obtained under thermooxidative conditions (heating in air at 80°C/min). Micrographs were obtained from gold-palladium-coated specimens.



(a)



(b)

Fig. 19. The morphology of the fractured char residue from (a) sample III and (b) sample II (fractured). Prepared in air at 80°C/min up to 750°C.

position occurs in an inert atmosphere, similar-looking char textures result among samples I (65 wt % DMS) and III (50 wt % DMS), with III exhibiting smaller “cell” dimensions. Both materials possess relatively porous structures. For the same magnification ($\times 80$), the char has more extensive smooth areas when the organic content of the residue is greatest as noted in sample II, Figure 18(b).

In a thermooxidative environment (air), a cellular structure is evident in sample I, Figure 18(a), and somewhat distended smoother areas are also noticeable here. This texture is in keeping with the morphology of sample II, Figure 18(b), which appears to possess a more compact char than either samples I or III [see sample II, Figure 17(b)]. In the air-oxidized residues, cracks are more evident than in the nitrogen pyrolysates. For instance in sample III, Figure 18(a), the cracks suggest that higher thermal stresses may have developed during decomposition reactions. Figure 19(a) also shows a micrograph of another area of sample III where the stresses may have been dissipated, without causing severe fracture, through “coiling” of the residue during degradation. In Figure 19(b),

TABLE VII
Ratio^a of Si in Chars Formed in Nitrogen (N) and Air (A) to Si in Original Copolymers (P)

Ratio	Sample no.		
	I	II	III
Si(N)/Si(A)	1	1.3	0.92
Si(A)/Si(P)	1 (1)	4.5 (4.0)	1.7 (1.6)
Si(N)/Si(P)	1 (1)	5.8 (5.1)	1.6 (1.5)

^a For EDAX peak heights appropriately normalized.

a less porous texture is found. Elsewhere,¹ in degradative experiments it has been stated that void contents in the range 75–90% are commonly found and that the macroscopic char density usually increases with the DMS content for the BPAC/DMS copolymer system. Conclusions dealing with the morphology of these chars are somewhat tenuous, since artifacts can undoubtedly arise during sample handling and preparation for analysis.

Silicon Residues

Since silicone is the only element that is readily amenable to energy dispersive X-ray, analysis with minimal disturbance to the chars, a comparison of Si counts (Figures 14 and 15) provides the relative silicone levels listed in Table VII. (All readings are normalized with respect to gold and Pd for the respective scales in the figures for identical counting times.) A strong correlation between Si in the residue and Si in the virgin materials is not evident, thus indicating that significant differences arise under inert and oxidizing conditions. As the DMS content is increased in these copolymers, more volatile cyclics are produced. Crosslinked structures must therefore feature in the reaction products as hydrogen abstraction reactions occur at higher temperatures. As a consequence, C—C linkages from methyl groups in DMS as well as BPAC fragments have been found¹ in some chars. The fact that the Si residue ratios in Table VII do not show a strong correlation with the Si or DMS content of the original copolymers suggests that complex reactions take place under the fast heating rates, 80°C/min, used in this comparison. In support of this complexity is the fact that a strong correlation is not found between the Si content of char residue (determined analytically) and the Si in the original polymers (see Table VIII).

In the review process, a referee indicated that the chemical structure of BPAC—DMS copolymers prepared by the method of Vaughn²⁷ was more complex than originally believed. Rather than consisting of a continuous molecular chain of random alternating sequences of bisphenol-A-polycarbonate and poly(dimethylsiloxane) blocks, sample I contains many isolated BPAC sequences connected chemically to PDMS. On the other hand, sample II is com-

TABLE VIII
Si Content of Char and Original Polymers (P)

Ratio	Sample no.		
	I	II	III
% Si(A ^a)	10.7	4.8	6.5
% Si(P)	24.7 (23.8)	9.5 (8.3)	19.0 (18.2)

^a A = air.

prised of PDMS blocks chemically linked to BPAC blocks. "Blockness" is therefore not so well defined as earlier work indicated, and the studies of Niznik and LeGrand²⁸ attest to this fact. Reevaluation of the residual silicon or silica based upon the most recent characterization data for these copolymers only marginally alters the results in Tables VII and VIII. The new values are bracketed in these tables, notwithstanding the limitations of the SEM/EDAX technique for quantitative measurements. The length and type of sequences undoubtedly influences the thermal degradation behavior which will be even more complex than if well-defined blocks existed in all of these BPAC/DMS materials. This situation is partly responsible for the lack of an obvious correlation between thermal stability and polymer composition.

The higher retention of Si noted for those copolymers with high BPAC content indicates that Char residue formation is more complicated in "inorganic" polymers than van Krevelan^{29,30} predicted for exclusively organic materials. As yet unknown but complex reactions, occurring within these copolymers, need to be investigated using infrared and GC/MS evaluation of the degradation process at different stages of decomposition.

CONCLUSIONS

(1) The thermograms show that two reactions are present in both air and nitrogen. At the lower heating rates there are distinctive, but they gradually merge when the rate is increased.

(2) In nitrogen, the activation energies for pyrolysis average about 44 ± 3 kcal/mol at lower temperatures. For higher decomposition temperatures, the latter values are attributed to unknown catalyzed reactions, the range from 11 to 27 kcal/mol.

(3) In air, activation energy values ranging from 28 to 35 kcal/mol were obtained.

(4) Oddly, the activation energy averages obtained for sample III are the highest.

(5) The thermal stability of the polymer, arbitrarily chosen as the temperature for 5% conversion, shows that all three samples behave similarly. In nitrogen, the values are about 50°C higher, i.e., 700 K compared to 660 K approximately.

(6) The Char yield depends upon heating rate and environment. Weight loss trends are noted between char levels and heating rates for the three copolymers. The silicone content in the residue is strongly dependent upon degradative conditions for a fixed heating rate. The char morphology also depends upon silicone content and DMS/BPAC ratio, but there is not a strong correlation between the Si content in residues and in corresponding virgin materials. More analytical work is required to establish the mechanisms of decomposition.

The authors express their appreciation to Dr. Roger Kambour for kindly providing the samples for this work. They are also indebted to Mr. George McManus for making the SEM measurements. Partial support by the Office of Naval Research is gratefully acknowledged.

References

1. R. P. Kambour, H. J. Klopfer, C. M. Orlando, and S. A. Smith, "Silicone Block Polymers: (1) BPF Carbonate-Silicone Block Polymers: Production of Optical Grade Extrudates and (2) Flammability of Silicone Block Polymers," Final Report, Contract #N0019-76-C-0096 for Naval Air Systems Command, Department of the Navy, July 1978.
2. J. M. Funt, D. Parekh, J. H. Magill, and Y. T. Shah, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 218 (1975).
3. H. M. Klimisch and R. C. Smith, in *Analysis of Silicones*, A. Lee Smith, Ed., Wiley-Interscience, New York, 1974, Chap. 6, p. 103.
4. T. H. Thomas and T. C. Kendrick, *J. Polym. Sci.*, **A2**, **7**, 537 (1969); **A2**, **8**, 1823 (1970).
5. F. E. McGrath, D. W. Dwight, J. S. Ruffle, T. F. Davidson, D. C. Webster, and R. Viswanathan, ACS Polymer Reprints, September 1979, Vol. 20, No. 2, p. 528.
6. J. Lipowitz, *J. Fire, Flammability*, **1**, 484 (1976); J. Lipowitz and M. J. Ziemelis, *J. Fire, Flammability*, **7**, 504 (1976).
7. N. Grassie and K. F. Francey, *Polym. Degradation Stability*, **2**, 53 (1980).
8. N. Grassie, K. F. Francey, and I. G. MacFarlane, *Polym. Degradation Stability*, **2**, 67 (1980).
9. K. A. Andrainov and A. I. Petrashko, *Russian Chem. Rev. (Engl. transl.)*, **38**(3), 211 (1969).
10. G. J. Knight, *Brit. Polym. J.*, **10**, 187 (1978).
11. A. Noshay and J. E. McGrath, *Block Copolymers*, Academic, New York, 1977, Chap. 7, pp. 335 et. seq.
12. A. D. LeGrand, G. G. Vitale, and D. G. LeGrand, *Polym. Eng. Sci.*, **17**(8), 598 (1977).
13. H. M. Li and J. H. Magill, *Polymer*, **19**, 829 (1978).
14. R. L. Merker and M. J. Scott, *J. Polym. Sci.*, **A2**, **2**, 15 (1964).
15. R. P. Kambour, J. E. Coon, H. J. Klopfer, S. Miller, C. M. Orlando, and L. D. Stang, "BPF Carbonate-silicone Block Polymers: Improved Synthesis and Further Studies of Mechanical and Flammability Properties," Technical Report #77CRD172, General Electric Co., August 1977.
16. A. Davies and J. H. Golden, *J. Macromol. Sci., Res. Macromol. Chem.*, **C3**(1), 49 (1969).
17. B. M. Kovarskaya, *Chem. Zvesti*, **18**, 13 (1964).
18. L. H. Lee, *J. Polym. Sci.*, **2**, 2859 (1964). H. W. Gibson, F. C. Bailey, and J. M. Pochan, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2499 (1979).
19. R. P. Kambour, W. V. Ligon, and R. R. Russell, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 327 (1978).
20. P. J. Lieu, J. H. Magill, and Y. C. Alarie, *J. Fire Flammability*, **11**, 167 (1980).
21. M. Kucera and J. Lamikova, *J. Polym. Sci.*, **54**, 375 (1961).
22. J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stds.*, **70A**, 487 (1966).
23. E. N. Peters, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C17**(2), 173 (1979).
24. A. D. Delman, M. Landy, and B. B. Simms, *J. Polym. Sci.*, **A1**, **7**, 3375 (1969).
25. S. Seymour and C. Robert, *J. Polym. Sci.*, **A1**, **4**, 2107 (1966).
26. M. G. Voronkov, V. P. Mileshevich, and Yu A. Yuzhelevsku, *The Siloxane Bond*, Leningrad, 1974, Chap. 3, p. 77, and *English Times*, Consult. Bureau, New York, 1979.
27. H. A. Vaughan, Jr., *J. Polym. Sci.*, **87**, 569 (1969).
28. G. E. Niznik and D. G. LeGrand, *J. Polym. Sci., Polym. Symp.* No. 60, 97 (1977).
29. D. W. van Krevelan, in *Properties of Polymers*, Chap. 21 and 26, Elsevier, Amsterdam, 1976, Chaps. 21 and 26.
30. R. P. Kambour, *J. Appl. Polym. Sci.*, **26**, 861 (1981).

Received June 1, 1981

Accepted July 13, 1981