Studies of the chemical degradation of polysiloxanes by hydrofluoric acid: (2). Poly-(tetramethyl-*p*-silphenylene siloxane-dimethyl siloxane) block copolymers

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Block copolymers of tetramethyl-*p*-silphenylene siloxane (TMPS) and dimethyl siloxane (DMS) have been selectively degraded with hydrofluoric acid solution. The HF preferentially attacks the Si–O bonds, particularly those of the non-crystalline DMS component. The copolymers which were precipitated by the self-seeding technique were etched with 48% HF at 30°C (established as suitable conditions for our work). The crystallinity change on etching these is largest for the sample of lowest TMPS content; it varies from about 20% at zero etching time to 98% after a period of 40 h approximately. The molecular weight, small-angle X-ray period, melting temperature, heat of fusion and degree of crystallinity were all determined as a function of etching time. The correlated results were found to be consistent with a two-phase model in which the DMS component was essentially excluded from the TMPS crystalline core. Some predictions, based on copolymer theories, were found to be consistent with the analysis of the experimental observations.

INTRODUCTION

Ever since the early 1960s selective chemical etching has proved to be a useful technique to probe the morphology of polymers. Mineral acids[1–15], ozone[16,17], alkaline materials[18–21] and even water[22,23] have been used for the purposes of degradation. However, all the literature reports known to the authors have dealt with homopolymers of wide and relatively narrow molecular weight distributions. Single crystals and bulk polymers have been examined. The narrowest distribution materials studied so far have been fractionated polysiloxanes and a report on this is pending publication[6]. Most of these papers have focused attention on the distribution of amorphous and crystalline material within a solution-grown crystal or bulk polymer. The defect nature of single crystals has been a controversial issue which chemical degradation has helped to a degree to elucidate. However, the precise morphological details of crystalline polymers are still unsettled[24–27].

Hydrofluoric acid (48%) at 30°C has provided a useful chemical probe to gain definitive knowledge about the distribution of ordered and 'amorphous' material in TMPS homopolymers[6]. The reagent is highly selective with minimal side reactions. An obvious extension of this work is to the copolymer field where TMPS is one of the components. The TMPS/DMS copolymer system having different weight ratios, but the same block size of DMS in different compositions, provides a unique system for study. The results of the application of an acid etchant to elucidate the morphology of such copolymers represent a novel step in the application of chemical reagents to elucidate the polymer morphology of complex thermoplastic materials (block copolymers).

Elsewhere the morphology of TMPS/DMS polymers has been studied in some detail by electron microscopy[28], scanning electron microscopy[29] and X-ray[28] methods. The present study both complements and extends this earlier work, providing a more detailed understanding of the chemical and physical composition and phases in these siloxane copolymers.

EXPERIMENTAL

Materials

Samples of tetramethyl-*p*-silphenylene siloxane–dimethyl siloxane copolymer (TMPS–DMS) were kindly supplied by Dr K. Polmateer of the Dow Corning Corporation. Samples were carefully crystallized from ethyl acetate–methanol mixture before characterization by g.p.c. and n.m.r. molecular weights were found to be between 10^5 and 10^6 and the mean block size of the non-crystallizable DMS component was 30 before copolymerization with the TMPS diol. The three polymers A, B and C used in this study have weight ratios of TMPS/DMS of 85/15, 65/35 and 48/52 respectively.

Procedure

The three copolymers were each crystallized from 0.1% solution mixture of ethyl acetate and methanol (volume ratio 2/1) using the self-seeding method described in the literature[28]. The solvent was removed from the samples *in*

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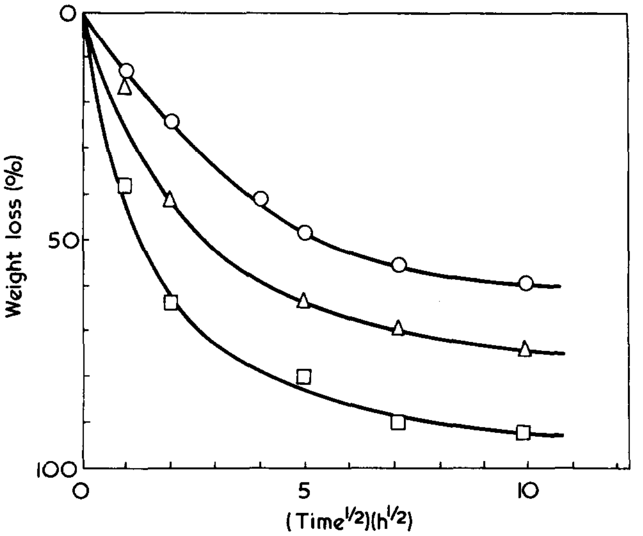

Figure 1 Percentage weight loss of TMPS–DMS copolymer on etching time (h) with 48% HF at 30°C. ○, copolymer A; △, copolymer B; □, copolymer C

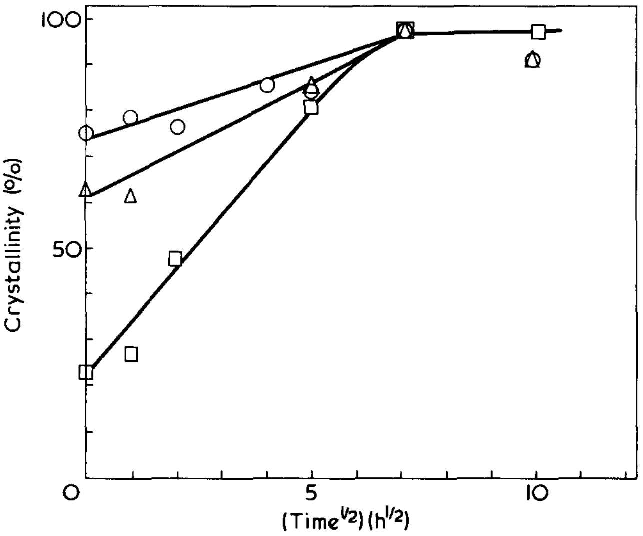

Figure 2 TMPS content of the copolymer (calculated from H n.m.r.) vs. etching time with 48% HF at 30°C: ○, copolymer A; △, copolymer B; □, copolymer C

vacuo at room temperature. Selective chemical degradation measurements were carried out at 30°C by the treatment with 48% HF as described for the TMPS homopolymer in a recent paper[6] (part 1 of this series). Weight loss measurements with time of degradation were conducted for periods ranging from minutes up to, and sometimes in excess of, 100 h. Changes in the copolymer composition[30] during the HF treatment were monitored by a proton n.m.r., 50 MHz, Varian Instrument. Molecular weights and molecular weight distributions were obtained by conventional g.p.c. analysis using a Water Associates g.p.c. unit. The aim of the present paper is to characterize, from a morphological point of view, the copolymer crystals of poly TMPS–DMS of three different compositions, and to provide meaningful correlations between chemical composition, morphology and physical parameters with the kinetics of degradation and tetrahydrofuran as a solvent. Aliquots of 0.5 ml of 0.25 % (w/w) polymer solution in tetrahydrofuran were injected into a series arrangement of four standard columns having porosity ratings of 3×10^6, 1.5×10^5, 10^4, 10^3 Å. Melting temperature and heat of fusion data were obtained on the original copolymer and degraded samples by Perkin–Elmer (d.s.c.) Calorimetry. An X-ray small-angle scattering unit (Rigaku–Denki) was used for determining the crystalline long spacing. Wide-angle X-ray measurements* were also made with GE (XRD5) equipment.

RESULTS

Figure 1 shows the weight loss of the three copolymers (A,B,C) as a function of time when selectively degraded with 48% HF at 30°C. It is found that the extent of weight loss increased as the DMS content in the copolymer increased and the curves show a levelling-off after many hours of reaction. The weight losses determined for these copolymers (A,B,C) corresponded to levels of 60, 74 and 92% respectively after about 100 h reaction time. *Figure 2* illustrates how the TMPS content (% w/w) in the copolymers increases linearly with time. After the specified treatment time with HF, the TMPS content was derived from H n.m.r. measurements at different stages of the degradation. When the TMPS level reached 100% it was assumed that all the DMS comonomer units were completely etched away from the copolymer crystals. The copolymer chain lengths, A_p, were measured by g.p.c. and the g.p.c. peak chain lengths, A_p, were calibrated with the standard polystyrene samples and poly TMPS fractions whose molecular weight were determined by light scattering and viscosity methods[31,32]. At this point in the investigation it is still difficult to estimate accurately the copolymer molecular weight since the Q values from the relationship ($M_p = Q^*A_p$) are not known for the copolymer samples and are changed with the degradation. *Figure 3* shows how the g.p.c. peak chain lengths decrease with the time of HF treatment. There is very little difference in the chain lengths among the three copolymers (A,B,C) at long treatment times when they are degraded with HF and the chain lengths reach about 130 Å in each case. Typical g.p.c. traces illustrated in *Figure 4* for the degraded copolymer C show only a single peak when refractive index difference is plotted against the elution volume. The chain length distribution (equivalent to the molecular weight dis-

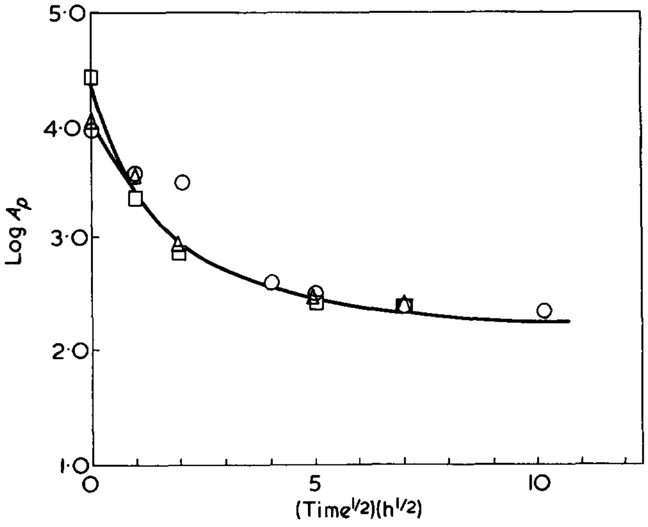

Figure 3 Plot of the g.p.c. peak molecular chain length, A_p, against treatment time for the copolymers degraded at 30°C with 48% HF: ○, copolymer A; △, copolymer B; □, copolymer C

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* A detailed report on this work describing a novel technique for crystallinity determination will be the subject of a later publication.

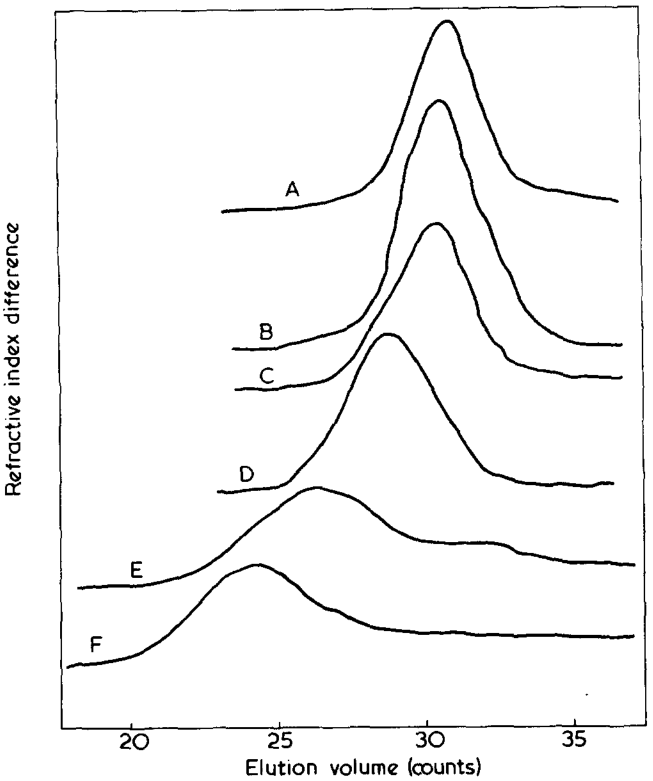

Figure 4 G.p.c. traces of copolymer B (TMPS/DMS: 65/35 % w/w) degraded with 48% HF at 30°C for various periods of time: A, 98 h; B, 51 h; C, 25 h; D, 4 h; E, 1 h; F, 0 h

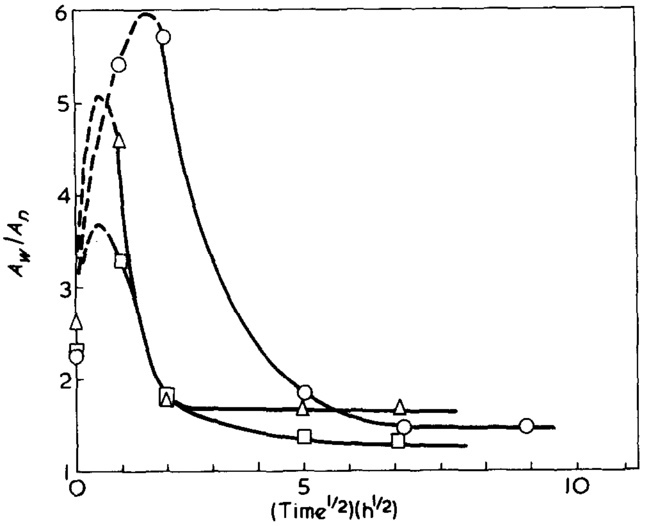

Figure 5 Plot of the molecular chain length distribution (A_W/A_N) as a function of degradation time with 48% HF at 30°C: ○, copolymer A; △, copolymer B; □, copolymer C

tribution) was ascertained from the spread of the g.p.c. peaks for different extents of reaction. In *Figure 5* the g.p.c. chain length distribution ($A_W/A_N = M_w/M_n$) of the resultant g.p.c. curves are plotted against the square root of time. At the beginning or during the early stages of the degradation, the molecular weight distribution of the copolymer specimen broadens initially with reaction time when a few polymer chains have been cut. For this reason the ratio A_W/A_N increases at first and then decreases as the distribution narrows with prolonged treatment time. It is worth noting that the curves tend to plateau soon after the polymers receive 25 h of treatment. Crystalline stem lengths determined by small-angle X-ray scattering as a function of HF treatment time are shown in *Figure 6*. A relatively small change in the long period was noted for copolymer A but a significant drop in long spacing occurs with time during degradation of the copolymer C which has the highest DMS content. The change in copolymer B is intermediate, but it is worth noting that the long spacings for all the copolymers (A,B,C) attain a common value around 66 Å.

Plots of the d.s.c. melting peak temperature vs. the treatment time are shown in *Figure 7*. For copolymers A and B, the measured melting temperatures decrease slowly with degradation time, but for copolymer C (highest DMS content) the observed melting temperatures for all these copolymers (A,B,C) reach a common value of approximately 120°C. Crystallinity levels (see *Figure 8*), based upon heat of fusion results, were also found to increase at long treatment times, the curves levelling off in the region of 90% or so after about 50 h degradation. The degree of crystallinity for copolymer C is found to increase substantially from nearly 20% to around the 90% level in this same period of time.

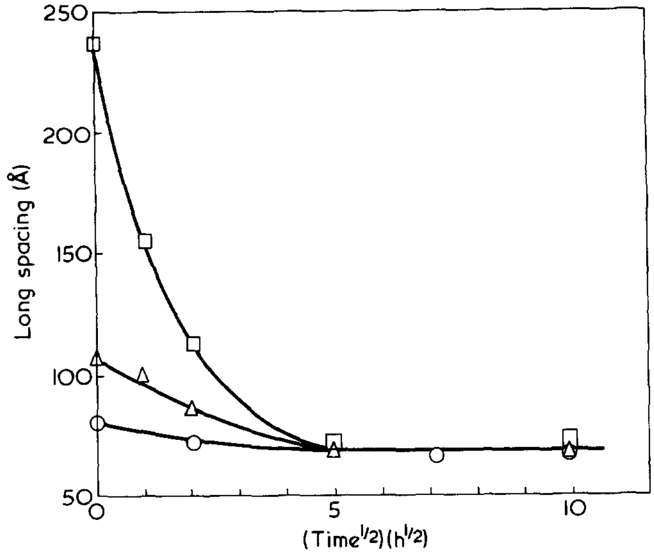

Figure 6 Dependence of X-ray spacing on etching time with 48% HF at 30°C: ○, copolymer A; △, copolymer B; □, copolymer C

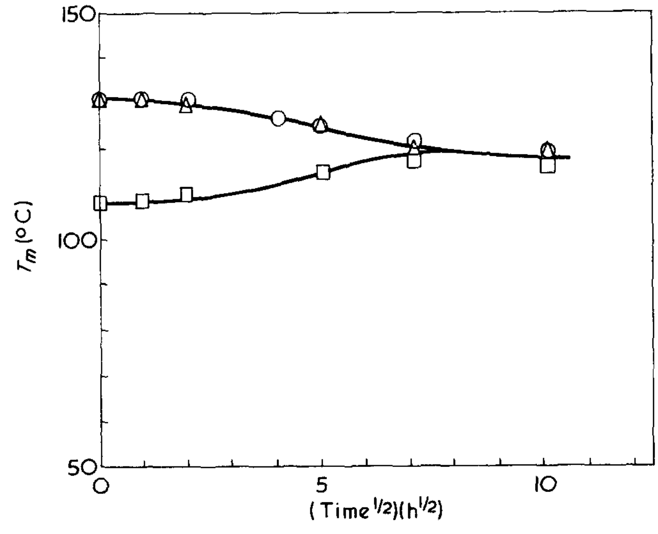

Figure 7 D.s.c. melting temperature peak of degraded copolymers A, B and C of original composition of 85/15, 65/35 and 48/52 % w/w respectively: ○, A; △, B; □, C

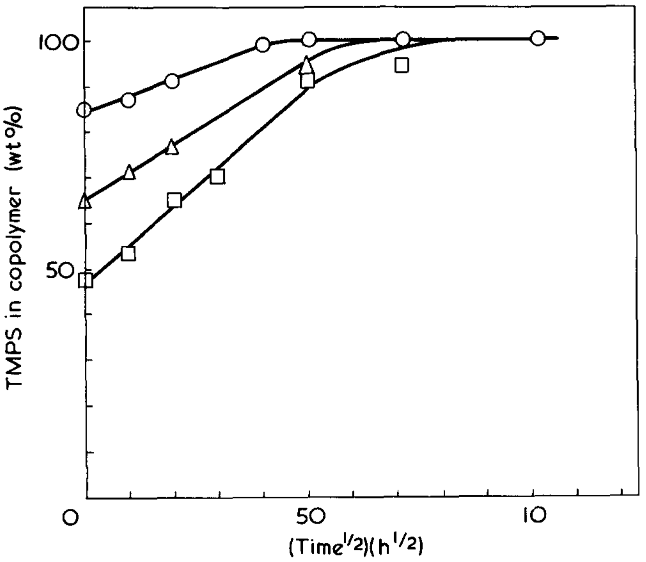

Figure 8 Percentage crystallinity (based upon d.s.c. heat of fusion) for the three copolymers. ○, A, 85/15 % w/w TMPS/DMS; △, B, 65/35 % w/w TMPS/DMS; □, C, 48/52 % w/w TMPS/DMS

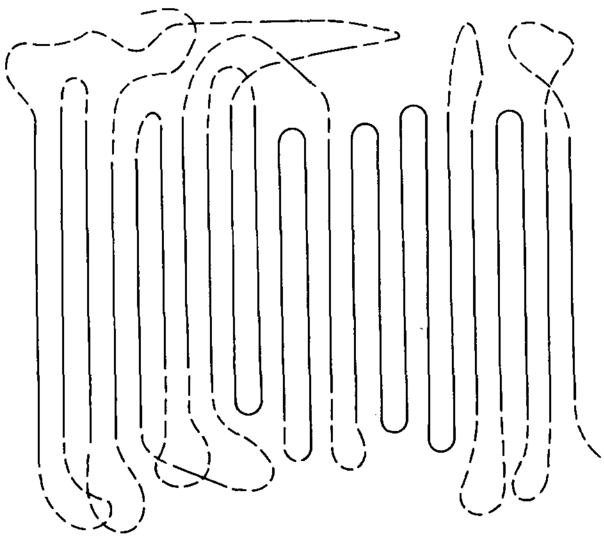

Figure 9 Schematic illustration of the TMPS/DMS model depicting amorphous DMS loops and crystalline TMPS core material. Short TMPS non-crystallizable sequences are also shown trapped between larger DMS sequences

DISCUSSION

The overall weight loss of the TMPS–DMS copolymers, determined by selective etching (or degradation) with HF, increases as the DMS component is increased. This behaviour is clearly illustrated by the results of *Figure 1*. The observed weight loss is mainly attributed to amorphous material removed from the surfaces of the copolymer crystals. A schematic illustration of the copolymer crystal model is given in *Figure 9*. A similar one reported elsewhere[29] is analogous to that invoked by Lotz and Kovacs for the block copolymer ethylene oxide–styrene[33]. The amorphous phase comprises mainly DMS sequences with minor contribution from short lengths of TMPS that have been trapped between DMS blocks in the chain during the synthesis. These TMPS sequences are too small to crystallize and so they are excluded from the main crystalline core (presumably as in the model illustrated in *Figure 9*).

Plots of the ratio of the molecular chain length of the etched to the original length as a function of specimen weight loss suggest that the molecular length is drastically decreased after about 20% weight loss. Thereafter, the polymer chain does not change very much during the substantial drop that occurs subsequently. This observation can be explained in the following way. In the early stage of etching, HF acid cuts the copolymer chains sporadically on the vunerable crystal surface with little or no chain unzipping taking place. After most of the surface material is cut, degradation occurs through chain unzipping, at a measurable rate, along each amorphous chain until it reaches the crystalline core. The weight loss of the DMS and/or TMPS chain component(s) in the amorphous part of the copolymer during this selective chemical etching process can be calculated from the data in *Figures 1* and *2*. The results of this analysis (*Figure 10*) show that the weight loss of DMS as a function of time is almost the same among the three copolymers. The DMS components of the chain are almost completely removed by the HF after approximately 25 h of reaction time. Contrast, however, the fact that TMPS weight losses in each copolymer give different curves and level off after about 52% for sample A, 60% for sample B and 85% for sample C. The extent of the weight loss attributed to TMPS is very much dependent upon the copolymer composition, and this loss increases as the mean TMPS chain sequence length in the copolymer decreases. That is, when the TMPS content in the copolymer is comparatively large the average sequence length of crystallizable units (TMPS) exceeds by far the critical crystallizable chain length that is required to form (or participate in) the crystalline (core) lamellae. Most of the amorphous phase is ascribed primarily to DMS. When the TMPS content is less abundant, some of the crystallizable sequence lengths tend to be shorter than this critical length so that the amorphous phase now comprises the DMS chain plus those shorter TMPS sequences that are trapped between the amorphous DMS blocks. At long etching times, therefore, the residual crystalline core of the copolymers becomes almost entirely crystalline, reaching levels of 98% crystallinity, a long period morphology of 66 Å, and a melting temperature of approximately 120°C. Note that the original copolymers crystallize from solution with similar crystalline core sizes but with amorphous dimensions

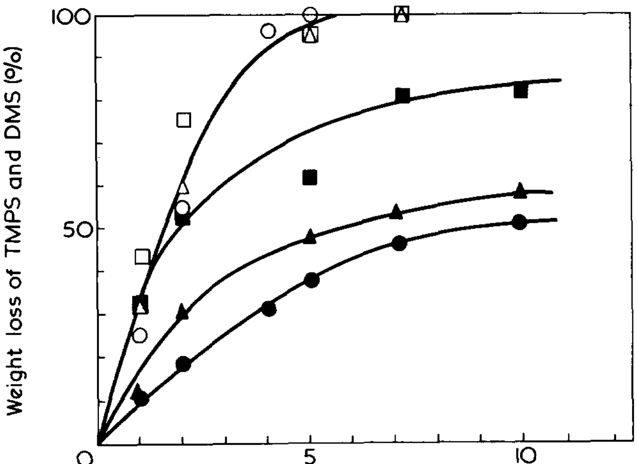

Figure 10 The relationship between the percentage weight loss of TMPS and DMS components for copolymers A, B and C as a function of etching time (h). ○, △, □, denote DMS losses; ●, ▲, ■, refer to TMPS losses (based on NMR estimates). ○, ●, refer to the 85/15 % w/w sample; △, ▲, to the 65/35 % w/w sample; □, ■, to the 48/52 % w/w sample

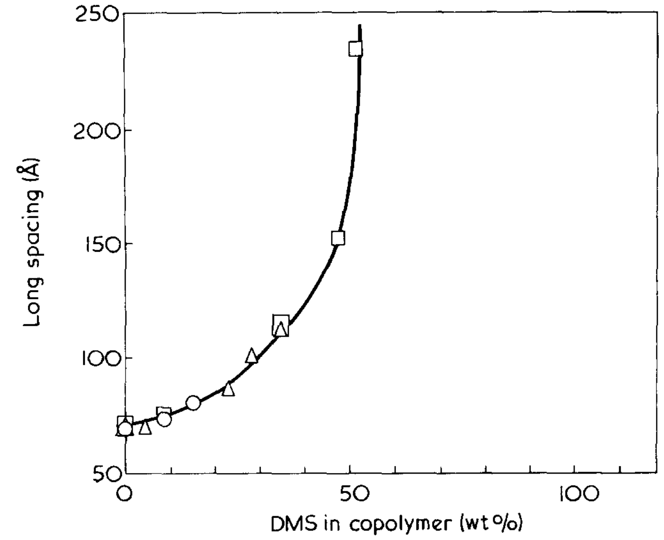

Figure 11 Long spacing (from small-angle X-ray scattering) *versus* DMS in copolymers (expressed as % w/w). Symbols represent compositions as above

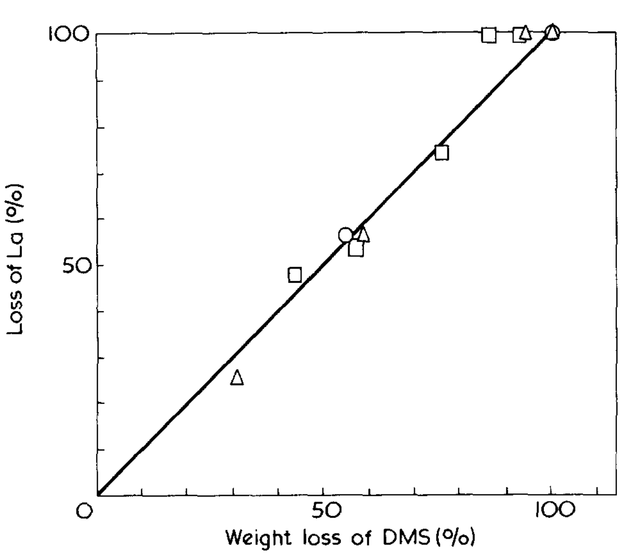

Figure 12 Loss of amorphous surface component, l_a (%) *versus* weight loss of DMS (%) for the three copolymers etched for different times with 48% HF at 30°C

that are drastically different (see, for example, *Figure 6*). Removal of this amorphous surface material causes an increase in crystallinity concomitant with a decrease in the long spacing, reflecting discrete changes in sample morphology. *Figure 11* demonstrates how the long spacing is affected by the DMS content of the copolymer. A dramatic upswing in small-angle spacing is noted as the amorphous component in the polymer chain is increased. (Similar results[35] were obtained for another series of TMPS–DMS copolymer samples having a DMS block size of 18 units.) The extrapolated value of the measured long spacing to zero DMS content corresponds to 66 Å. If it is now assumed that the crystalline core (see *Figure 9*) is 66 Å for the three copolymers (A,B,C), the decrease in the amorphous spacing may be calculated from equation (1):

$$\text{Relative decrease in amorphous spacing} = \frac{l_0 - l_t}{l_0 - l_c} \qquad (1)$$

where l_0 is the long spacing of the original copolymer crystal, l_c is the length of the crystalline core, and l_t is the value of the long spacing after degradation time, *t*. *Figure 12* shows the relation between the weight loss of the DMS component and the decrease in amorphous spacing calculated on this basis. Good correlation is found between the decrease in long spacing and the loss in DMS (% w/w) in the copolymers with degradation time. This result strongly supports the notion that the amorphous DMS component controls, in large measure, the long spacing which seems to comprise a fixed crystalline core with a variable amorphous contribution. This argument does not violate the existence of an average DMS block sequence. Indeed, from copolymer theory[34], it can be shown that the mean sequence-length of TMPS is about 60 for copolymer A, 20 for copolymer B, and 10 for copolymer C. Since the crystalline core of the copolymers is 66 Å (i.e. 8 to 9 TMPS monomer units), it can now be demonstrated how the copolymer composition is related to the weight loss, long spacing and degree of crystallinity of the copolymer. If the TMPS mean sequence length falls below 8 monomer units, the copolymer would not be crystallizable (i.e. an amorphous copolymer would be anticipated).

Using the data of *Figure 1* the limiting weight losses for the three copolymers are now plotted in *Figure 13*. Note that the curve comprising this data extrapolates to a TMPS level in the copolymer of 40% w/w based on TMPS. Again, when the degree of crystallinity of the original copolymer is plotted graphed as a function of TMPS content (expressed in % w/w), the data also extrapolate to a 40% w/w limit of TMPS in the copolymer. Using this extrapolated value for the copolymer composition (i.e. 40/60) the sequence length of the TMPS component can be derived on the basis of random copolymer theory[34]. A mean sequence length corresponding to 8 TMPS units is calculated in good agreement with the above assumptions. The siloxane copolymer of 40% TMPS content has a mean TMPS sequence length about 8.

Note that there is an apparent discrepancy between the g.p.c. A_p limit of 130 Å (*Figure 3*) and the stem length derived from small-angle X-ray scattering (*Figure 6*) which is 66 Å after similar etching times. This two-fold difference in chain length can be explained by the fact that the small-angle measurement only reflects the sample morphology,

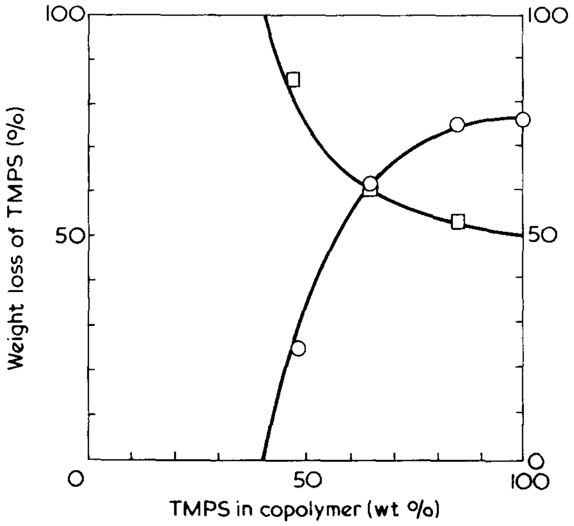

Figure 13 (a) Weight loss (%) of TMPS (by n.m.r.) *versus* weight percent TMPS in copolymer for various etching times with 48% HF at 30°C. (b) Crystallinity (%) *versus* weight TMPS (%) in polymer (by n.m.r.) for the same conditions as (a). The symbols ○, △, and □ depict original copolymers A, B and C respectively

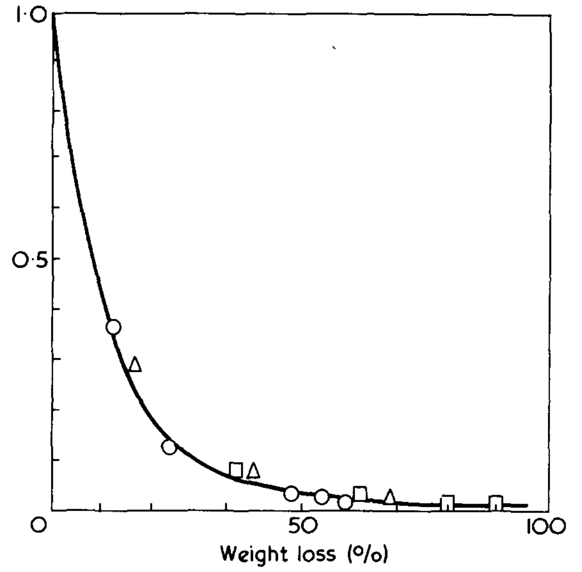

Figure 14 Plot of A_p/A_{p0} (ratio of degraded chain length at time *t* to the original or undegraded length) vs. weight loss (%) for all three copolymers using 48% HF solution at 30°C

not the chain length. For instance, both single and double traverses may exist in the crystal residue with only a single long period corresponding to the average stem or core length in the degraded sample. On the other hand, the g.p.c. chain length A_p of *Figure 3* is closely associated with the weight-average molecular weight, and consequently more strongly emphasizes the longer chains in the degraded specimen. This particular suggestion is currently under close scrutiny and the latest preliminary results[36] with high-resolution g.p.c. (at the University of Bristol, UK) indicate that both singlet and doublet peaks may be overlapped in the residue although single stems only are expected at long etching times. Details of this work will be reported later.

CONCLUSIONS

TMPS–DMS copolymers of different compositions can be selectively degraded by 48% HF solution at 30°C.

Acid degradation occurs predominantly in the more vulnerable DMS amorphous phase that resides outside the crystalline TMPS core in solution-crystallized specimens of varying composition.

A self-consistent morphological picture of the two-phase nature of these TMPS–DMS copolymers can be obtained using several complementary techniques: small-angle X-ray, g.p.c., n.m.r. and d.s.c.

The behaviour of these siloxane random block copolymers is consistent with theory. A lower limit to the TMPS sequence length is predicted for a crystallizable TMPS/DMS copolymer.

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