polymer papers

Gamma radiation effects in a modified poly(methyl methacrylate): Dielectric properties

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Contour maps of dielectric loss tangent within the ranges 0.01 Hz to 3 MHz and −150°C to +195°C, together with d.c. conductivity data above ambient temperature, are presented for a commercial poly(methyl methacrylate) modified by the addition of 15% by weight of triallyl cyanurate, both before and after γ-irradiation. Corresponding reference data is presented for the unmodified and unirradiated poly(methyl methacrylate). Of the three principal dispersions, the β-dispersion is the least affected by the addition of the cyanurate and by irradiation of the modified material. Evidence for two additional processes associated with the cyanurate is presented.

(Keywords: dielectric loss; poly(methyl methacrylate); gamma radiation; degradation; crosslinking; additives)

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been widely employed in industrial and domestic applications since it was first commercialized in 1931. PMMA is generally regarded as typical of that class of polymer which undergoes chain scission without the simultaneous formation of crosslinks when exposed to ionizing radiations[1–5]. Mechanisms for protection against radiation-induced chain scission have been noted by various workers[1,2,4], some of whom have succeeded in producing modified PMMA in which crosslinks between adjacent PMMA chains are formed (for example, see ref. 4). Allyl compounds appear well suited to protection by the promotion of crosslinking and, in an earlier study[6a], dynamic mechanical measurements were used to investigate the influence of ^{60}Co γ-radiation on the behaviour of PMMA modified by the addition of 15% by weight of triallyl cyanurate (TACN).

In view of the behaviour noted during the latter study[6a], particularly the rise of the glass transition temperature T_g with radiation dose, it was considered worthwhile to investigate the same PMMA/TACN composition using the dielectric method with its attendant advantage of a wider frequency range. As TACN contains polar groups, the use of the dielectric method raises the possibility of dispersions specific to TACN which may then be monitored as irradiation proceeds. The present study encompasses radiation doses sufficient for the underlying process of PMMA chain scission to become apparent.

EXPERIMENTAL

Sample preparation

15% by weight of TACN was mixed with I.C.I. 'Diakon' grade MG2 clear moulding pellets of PMMA. The mix was heated to 175°C for a few minutes before being milled at the same temperature and then pressed into sheets at 190°C. A sheet of unmodified reference PMMA was prepared in the same way but without TACN. Three sheets of the modified PMMA were exposed to γ-radiation from a ^{60}Co source (0.158 Mrad/hour) for varying times to give samples which had received total radiation doses of 20, 30 and 40 Mrad. Subsequently, sheet thickness was reduced to between 0.3 and 0.5 mm by pressing at 190°C.

Specimens for the dielectric and d.c. conductivity measurements were produced by painting colloidal silver on opposite faces of samples cut from the sheets to form matching rectangular electrodes about 200 mm^2 in area. Typically, the capacitance of an air gap capacitor of equivalent geometry fell within the range 3 to 5 pF.

Dielectric and d.c. conductivity measurements

Dielectric measurements were obtained using the wide-band permittivity bridge of Pratt and Smith in its original form[7]. Real and imaginary components of complex permittivity corresponding to loss tangents in excess of 0.001 were recorded within the ranges 0.01 Hz to 3 MHz and −150°C to +195°C. We note that performance parameters for the bridge have been improved since the present measurements were completed[8]. In particular, the minimum measurable loss tangent has been reduced to 0.0003 and the accuracy above 1 MHz has been increased.

The measurements of d.c. conductivity were obtained using a Keithley Instruments type 602 electrometer in the current mode together with a stabilized high-voltage supply. Care was taken to allow sufficient time to exclude the influence of transient currents.

RESULTS

The dielectric response of unmodified PMMA is shown in *Figure 1* as a temperature–frequency contour map for the loss tangent (tan δ). Comparable tan δ maps for the

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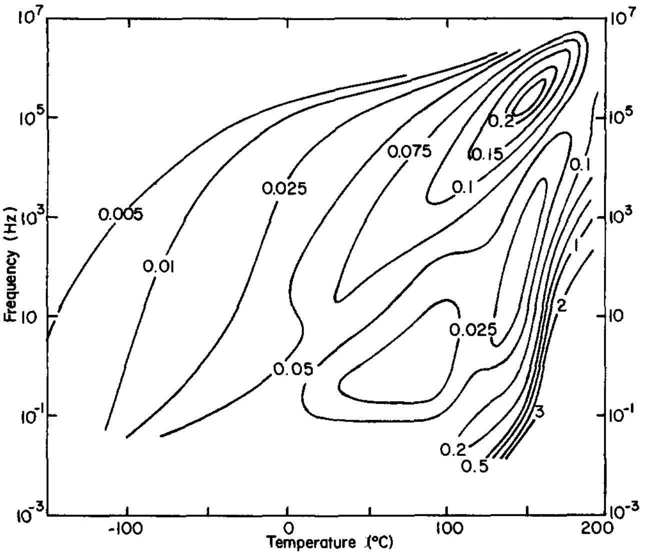

Figure 1 Contour map showing the temperature–frequency variation of the dielectric loss tangent (tan δ) of unmodified PMMA

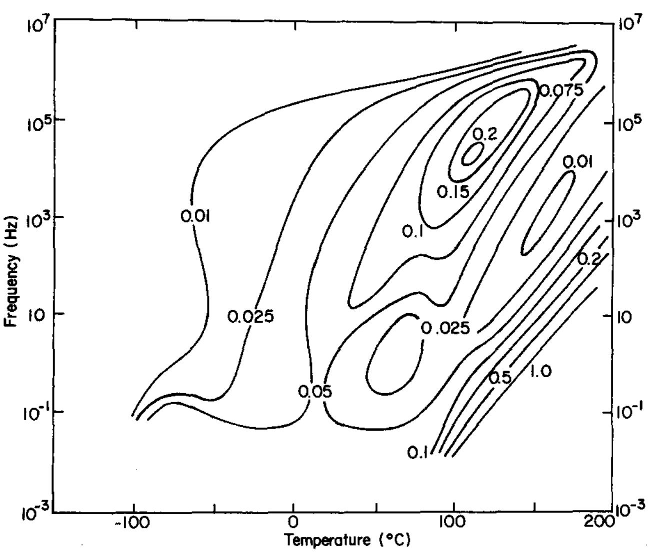

Figure 2 Contour map of tan δ for PMMA modified by the addition of 15% by weight of TACN

unirradiated and irradiated (30 Mrad) specimens of PMMA modified by the addition of 15% by weight of TACN are shown in *Figures 2* and *3* respectively. *Figure 4* shows the variation of tan δ with temperature at 10 Hz and includes data from the specimens irradiated to 20 and 40 Mrad in addition to points extracted from *Figures 1* to *3*.

Three distinct regions are common to each curve of *Figure 4*. There is a broad loss peak centred around 36°C, a more sharply defined peak of similar maximum intensity located variously within the range 93°C to 123°C and a region at the highest temperatures where tan δ increases rapidly with temperature. No substantial variation occurs in the shape or maximum intensity of the broad peak. The temperature location of the peak is also substantially unaffected, except possibly at the highest radiation dose. The broad peak is identified as the β-relaxation. In contrast, the addition of the TACN causes a significant shift (−30°C) in the temperature location of the sharp peak. This peak is identified as the α-relaxation and is associated with the glass transition. Irradiation of the polymer tends initially to counter the shift in the location of the sharp peak caused by the addition of TACN, as shown in curve A of *Figure 5*. *Figure 5* also shows the variation of T_g with radiation dose for both modified (curve B) and unmodified (curve C) PMMA reported previously[6] using a low-frequency mechanical torsion pendulum at 0.2 and 0.3 Hz respectively. The high temperature region of rising tan δ in *Figure 4* is identified with an interfacial process which may be described by the Maxwell–Wagner–Sillars (MWS) equations.

A more complete picture of the dielectric response of the materials is provided by *Figures 1* to *3*. For the unmodified PMMA (*Figure 1*) the β-relaxation may be seen as the broad region of substantial loss extending from about 0°C at 0.1 Hz to about 170°C at 1 MHz. The sharper and weaker α-dispersion occurs in the range 110°C to 130°C, and merges significantly with the β-dispersion above about 1 kHz. The MWS-process is apparent as a low- to medium-frequency loss which rises to very high values above about 130°C.

The addition of TACN to the PMMA (*Figure 2*) influences the β-dispersion only marginally but shifts the α-dispersion to lower temperatures so that it now occurs in the approximate range 80°C at 0.1 Hz to 110°C at

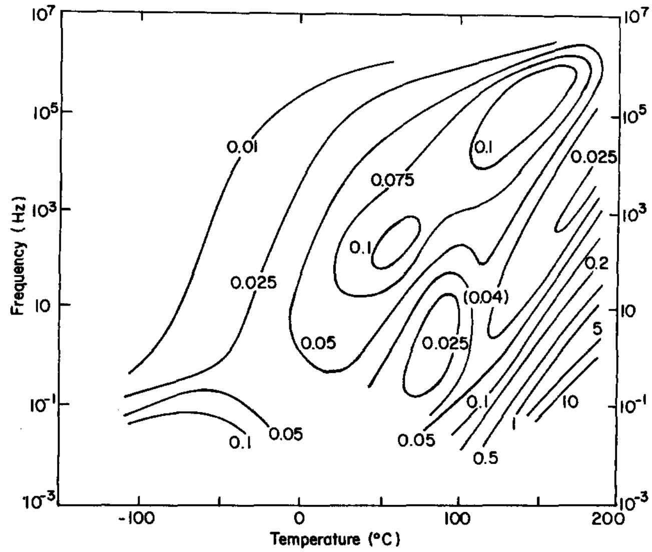

Figure 3 Contour map of tan δ for PMMA/15% TACN after exposure to 30 Mrad of ^{60}Co γ-radiation

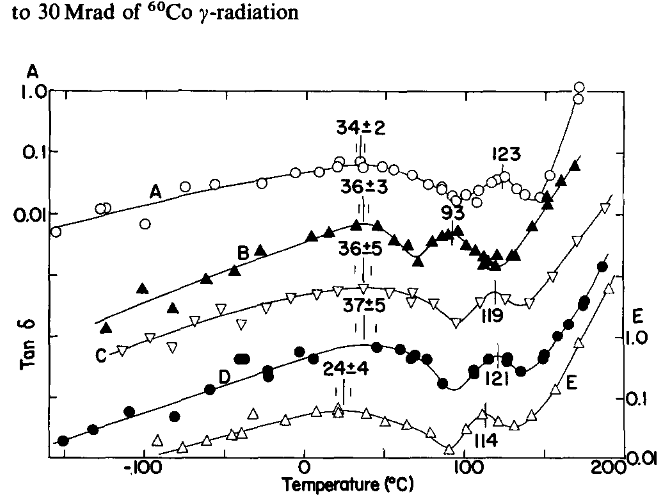

Figure 4 Variation of tan δ at 10 Hz with temperature for (A) unmodified PMMA, (B) PMMA modified by the addition of 15% by weight of TACN, (C) PMMA/15% TACN after 20 Mrad γ-irradiation, (D) PMMA/15% TACN after 30 Mrad γ-irradiation, (E) PMMA/15% TACN after 40 Mrad γ-irradiation

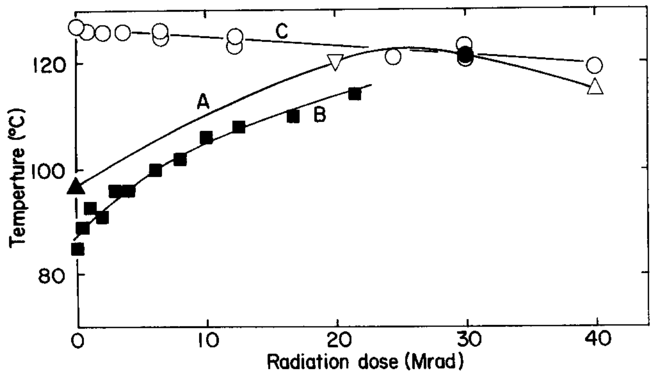

Figure 5 Variation with γ-radiation dosage of (A) the temperature of the high-temperature peak (associated with T_g) of curves (B) to (E) in *Figure 4* for PMMA/15% TACN at 10 Hz; (B) the glass transition temperature for T_g for PMMA/15% TACN at 0.2 Hz obtained with the torsion pendulum[6a]; (C) T_g for unmodified PMMA at 0.3 Hz obtained with the torsion pendulum[6b]

10 kHz. The slope of the MWS-process above 150°C is reduced. *Figure 2* also suggests the possibility of a loss peak of low intensity in the region of −70°C at 0.01 Hz arising as a consequence of the addition of the TACN. The process giving this peak will be referred to as the N1-process.

Following irradiation (30 Mrad) of the modified PMMA (*Figure 3*) the essential character of the β-dispersion is retained, although from about 20°C at 0.01 Hz to about 50°C at 100 Hz there appears to be an admixture of an additional loss. The process giving rise to the latter will be referred to as the N2-process. The α-dispersion in *Figure 3* may be seen to have shifted to higher temperature as indicated previously in *Figure 5*. The MWS- and N1-processes persist without any substantial alteration compared with the situation before irradiation.

Arrhenius plots of the frequency of the tan δ peaks against reciprocal temperature are shown in *Figure 6* for each of the principal processes in the materials studied. The gradients of the individual plots are used to calculate an apparent activation energy for each process. An average value of 94±7 kJ mol^{-1} is obtained for the activation energy of the β-relaxation in both unmodified PMMA and PMMA containing TACN. *Table 1* gives values of 75 to 126 kJ mol^{-1} for the same activation energy reported in the literature[9−28]. For the high-temperature low-frequency MWS-process an activation energy of 370±10 kJ mol^{-1} is obtained for the unmodified PMMA, compared with 163±8 kJ mol^{-1} for both the unirradiated and the irradiated PMMA containing TACN. Results for the α-relaxation are less unambiguously defined. In the plots of *Figure 6(a)* only the unmodified PMMA displays ideal linear behaviour. The overall average value of 700±100 kJ mol^{-1} compares favourably with values of 305 to 1045 kJ mol^{-1} which have been reported[21−29] for the α-process in poly(methyl methacrylate) (*Table 1*).

Figure 7 shows Arrhenius plots of d.c. conductivity against reciprocal temperature for unirradiated PMMA, both unmodified and modified, and for the representative γ-irradiated specimen (30 Mrad) of the modified material. The addition of 15% by weight of TACN increases the d.c. conductivity of the PMMA by one to three orders of magnitude. Conductivity falls with subsequent irradiation of the modified PMMA. 30 Mrad is sufficient to cause a two- to six-fold change, depending on temperature. The activation energy for conduction at the higher temperatures decreases from 210 kJ mol^{-1} for the unmodified PMMA to 132 kJ mol^{-1} for the modified PMMA before irradiation, increasing to 170 kJ mol^{-1} after 30 Mrad. In contrast, the activation energies at the lower temperatures vary only within the range 40 to 50 kJ mol^{-1}.

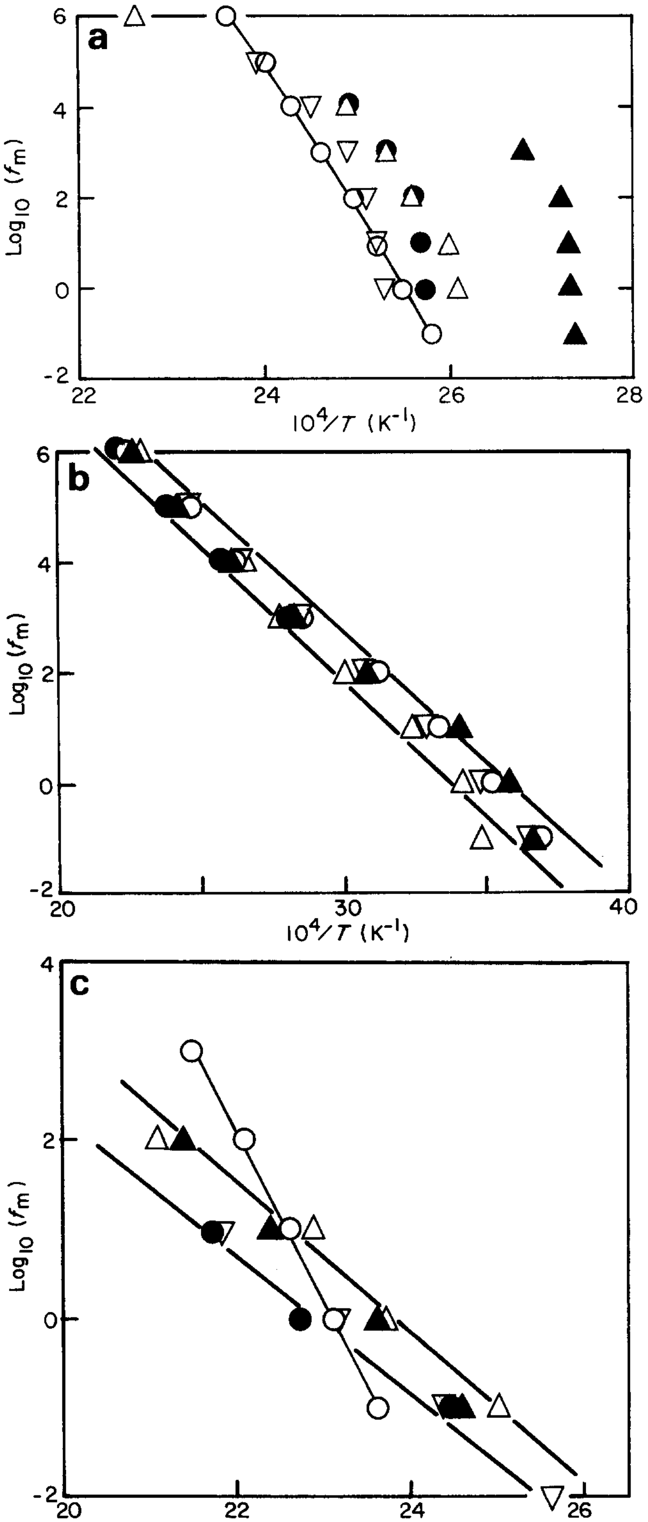

Figure 6 Arrhenius plots of the frequency of the tan δ peaks against reciprocal temperature for (a) the α-peak, (b) the β-peak and (c) the tan δ = 1.0 contour of the MWS-process. The symbol ○ refers to unmodified PMMA. The symbols ▲, ▽, ● and △ refer to PMMA/15% TACN after 0, 20, 30 and 40 Mrad γ-irradiation, respectively

Table 1 Literature values for activation energies (kJ mol^{-1}) of the α- and β-processes in PMMA. Values refer to dielectric measurements unless otherwise indicated as follows: m—mechanical, p—phosphorescence depolarization and t—thermally stimulated depolarization. Solunov and Ponevsky, 1977, also report values 71 to 126 kJ mol^{-1}

α	β	Reference
	88	Mead and Fuoss, 1942
477^{m}	88	Bröns and Müller, 1950
	109^{m}	Iwanagi and Hideshima, 1953
	75, 84	Deutsch *et al.*, 1954
	126	Sato *et al.*, 1954
	126^{m}	Iwanagi, 1955
420	75^{m}, 88^{d}	Heijboer, 1956
305	59	de Brouckere and Offergeld, 1958
	88	Mikhailov, 1958
	80	Ishida and Yamafuji, 1961
	76	Reddish, 1962
507		Lewis, 1963
	71, 73	McCrum and Morris, 1964
	80^{d}, 121^{m}	Saito, 1964
415 to 460^{d}	80 to 96^{d}	McCrum *et al.*, 1967
335 to 1045^{m}	71 to 126^{m}	McCrum *et al.*, 1967
	75	Thompson, 1968
1025	88	Sasabe and Saito, 1968
	90	Kawamura *et al.*, 1969
	111	Solunov and Ponevsky, 1977
	99	Lipatov, 1977
420	83	Hedvig, 1977
420±100	84±6	Gilbert *et al.*, 1977
	71 to 105^{d}, 50^{t}	Vanderschueren and Linkens, 1977
460±10	115±5^{p}	Rutherford and Soutar, 1978
	80	Mashimo *et al.*, 1978
700±100	94±7	Present work

DISCUSSION

Shultz[30], Charlesby and others[2,31] report that exposure of PMMA to γ-radiation at low temperatures results in main chain scission, rupture of side chains, and the introduction of double bonds into the polymer chain[2,32,33]. Geuskens and co-workers[34] argue that the macroradicals so formed have a very low probability of escaping from the cage formed by the surrounding polymer molecules. Thus, it is likely that they would react with radicals from TACN to form links with adjacent polymer chains.

The efficacy of TACN in promoting radiation-induced crosslinking of polymers has been reported by a number of workers[35–37]. Crosslinked copolymers which contain no linear polymer of TACN have been observed[37]. Gillham and Mentzer[38], Clampitt and others[35,36] report that homo- and copolymers of TACN are formed in two distinct steps. The first involves reaction of two of the three allyl groups in the TACN molecule and the second involves rearrangement of polymerized TACN plus reaction of the final double bond. Much of the polymerization must occur in the solid state. Furthermore, Gillham and Mentzer[38] report that, in air in the absence of an initiator, no discernible homopolymerization of TACN could be detected below 130°C nor any significant amount below 150°C. Indeed, even in the presence of 10% radical initiator no significant homopolymerization of TACN occurred below 120°C. They regarded this observation as further evidence that all reacted TACN was fully incorporated in an MMA/TACN copolymer.

The identification of the α- and β-relaxations assumed here is supported by the values obtained for their respective activation energies, both of which are in agreement with values reported in the literature (*Table 1*). It is generally agreed (see for example refs. 24, 25) that the α-process is directly associated with the glass transition and involves micro-Brownian motion of large segments of the main polymer chain. The shift of the α-peak to lower temperature on modifying PMMA by the addition of TACN (*Figures 1* and *2*) can be explained by the plasticizing action of the low molecular weight additive. Exposure of the modified PMMA to γ-radiation increases T_g to a maximum for doses between 20 and 30 Mrad, after which it decreases with further irradiation (*Figure 5*). Such behaviour closely parallels that reported by Pinner and Wycherley[4] for PMMA plasticized by diallyl sebacate. In each system, infra-red spectrophotometry confirms the occurrence of crosslinking in the range 0 to 20 Mrad associated with loss of allyl unsaturation[4,6]. Once depletion of allyl monomer is complete, continued irradiation causes further degradation of PMMA by chain scission, with a consequent lowering of the average molecular weight and a reduction in T_g.

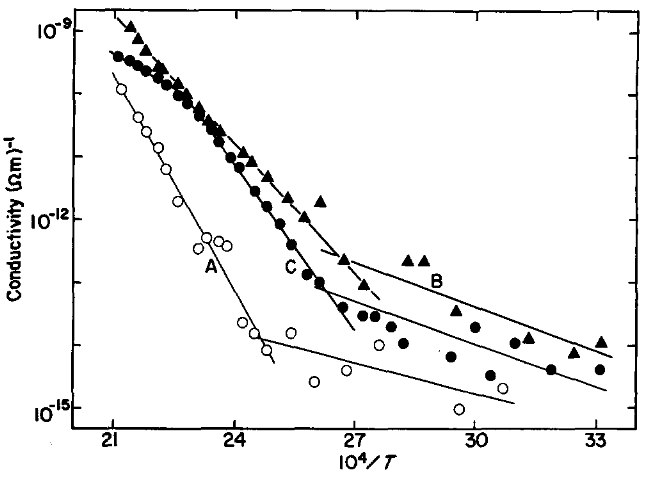

Figure 7 Arrhenius plots of d.c. conductivity against reciprocal temperature for (A) unmodified PMMA, (B) PMMA modified by the addition of 15% by weight of TACN, (C) PMMA/15% TACN after 30 Mrad γ-irradiation

Alternative explanations have been proposed regarding the nature of the molecular mechanisms associated with the β-relaxation in methacrylate polymers. One explanation entails a restricted motion of the polymer backbone[24]. An alternative, and more widely accepted view[11,20–23,39,40], is that the β-process involves hindered rotation, or other local motions, of the ester side group, with considerable interaction with the polymer backbone. Such motion would be substantially independent of gross motions of the polymer chains and unaffected by a low molecular weight additive such as TACN. Even a moderately high degree of crosslinking should not constrain significantly the motion of the ester side-group as the size of the TACN molecule is large compared with that of the side-group. The introduction of linkages would also tend to maintain the considerable free volume of the modified polymer, thereby reducing steric hindrance to side-group motion. The results of the present work are entirely consistent with these considerations in that they show that the β-relaxation in PMMA is essentially unaffected by modification with TACN and subsequent γ-irradiation, at least to 30 Mrad. Above 30 Mrad the reduction in average molecular weight caused by chain scission will create more free volume and reduce the steric hindrance to rotation of the ester side group, which may be expected to shift the temperature location of the β-peak at 10 Hz in the manner shown (curve E, *Figure 4*).

The N1-dispersion in the region of -70°C at 0.01 Hz (*Figure 2*) occurs on the addition of TACN and is not apparent in the unmodified PMMA (*Figure 1*). The dispersion persists after γ irradiation (*Figure 3*) without a marked change in integrated intensity. It is likely, therefore, to involve the core structure, that is the polar cyanurate groups, of the TACN molecule.

The N2-dispersion is seen in the $\tan\delta$ map of the modified PMMA after irradiation (*Figure 3*) as a change in the contour distribution compared with the unirradiated material (*Figure 2*) caused by the merging of the N2- and β-dispersions in the region from about 20°C at 0.01 Hz to about 50°C at 100 Hz. A qualitative appraisal of the extent of the admixture suggests an initial increase in the intensity of the N2-dispersion with irradiation followed by a fall in intensity beyond about 30 Mrad. This maximum in N2-loss intensity with irradiation parallels approximately the behaviour of T_g (*Figure 5*). The N2-process is tentatively associated with the formation of partially-complete links during irradiation of the modified PMMA. We postulate that the initial step in the radical-induced copolymerization is the production of end-links and/or partially-complete crosslinks between TACN and PMMA molecules. Additional γ-irradiation reacts further allyl groups in the attached TACN molecules to complete linkages between adjacent macromolecular chains. Any proposed mechanism for the N2-process within this model should involve a form of substantially independent motion of the linked TACN unit. In particular, the mode of motion should be different from that of the intra-molecular motion proposed for the N1-process and could, for example, involve rotational or wagging components. Initially, the intensity of the N2-dispersion would be expected to increase with radiation dose as links are formed. At higher radiation doses crosslinking of some of the individual TACN units would be completed. This would restrict the mobility of the linked TACN units and would lead to a reduction in the intensity of the N2-dispersion as fewer motile units remain. The approximately parallel behaviour of the shifts in T_g and in the intensity of the N2-dispersion with radiation dose suggests that a rotational motion of doubly-linked TACN units is the most probable cause of the N2-process. In addition, there appears to be no reason why intra-chain linkages should not also be formed by this means.

The major portion of the high-temperature, low-frequency dielectric dispersion is attributed to effects associated with interfacial or MWS-polarization. Intuitively, such effects might have been expected to be absent in a single phase amorphous polymer such as PMMA, even if it was anticipated that they might occur after modification by the addition of TACN. However, the unmodified material used in this study was not pure PMMA but a polymer of commercial origin. Furthermore, morphological structures have been reported even in amorphous materials[41–43], indicating that limited order exists in regions of such materials. Microscopic domains have been observed in PMMA in particular[44,45]. More specifically, on the basis of e.s.r. and n.m.r. studies, Murakami and Sohma[46] have reported the existence of two phases in PMMA. The MWS-polarization might, therefore, be associated with the presence of small ordered domains in predominantly amorphous poly(methyl methacrylate). Separate measurements confirm that d.c. conduction losses provide only a minor contribution towards the dispersion. The observed reduction in activation energy for the MWS-process in modified PMMA could be explained by an increased mobility of charge carriers within domains contributing to the MWS-polarization.

The variation in d.c. conductivity shown in *Figure 7* is consistent with initial plasticization on addition of TACN to PMMA and with subsequent formation of crosslinks during γ-irradiation. TACN may act in two ways. Conductivity is increased because the concentration of possible charge carriers is increased by addition of the polar TACN molecules, and also because the overall mobility is increased by their plasticizing action, as indicated by the reduction in activation energy. The more open structure of the modified (plasticized) PMMA facilitates the drift of charge carriers. In contrast, crosslinking by irradiation removes charge carriers and reduces the mobility of those remaining. Both factors reduce conductivity after irradiation.

CONCLUSIONS

A single apparatus has been used with solid specimens of smaller dimensions than is customary to study variations in the complex relative permittivity of modified PMMA within the ranges 0.01 Hz to 3 MHz and -150°C to $+195$°C. The three distinct dispersions observed in unmodified PMMA are attributed to the primary α-relaxation associated with the glass transition, the secondary β-relaxation involving the ester side-group and to an MWS- or interfacial polarization. Modification of the PMMA by the addition of 15% by weight of triallyl cyanurate plasticizes the structure, shifts the glass transition temperature to lower temperatures, approximately halves the activation energy of the high-temperature MWS-process and introduces a dispersion (N1) in the region of -70°C at 0.01 Hz which is thought to arise from the polar cyanurate groups within the TACN.

Subsequent γ-irradiation of the PMMA/TACN polymer tends initially to restore the glass temperature to high temperatures. Radiation doses above about 25 Mrad reverse this trend. Irradiation appears to have no substantial effect on the activation energy, in so far as it may be properly defined, of the α-relaxation of the modified PMMA or on the activation energies of the β-relaxation and the MWS-process. The N1-dispersion also persists with little apparent change after irradiation. γ-irradiation of modified PMMA does, however, appear to generate an additional dispersion (N2) which reaches its maximum intensity at a dose broadly comparable to that for the peak of the shift in the glass transition temperature. It is suggested that the N2-dispersion may be associated with a motion (distinctive in character compared with that causing the N1-dispersion) of linked TACN units.

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