

# Protective Effect of the Phenyl Group In $\gamma$ -Irradiated Compatible Blends of Poly(methyl Methacrylate) and Poly(styrene-Co-Acrylonitrile)

T. Q. NGUYEN and H. H. KAUSCH, *Laboratoire de Polymères, Ecole Polytechnique Fédérale de Lausanne, CH-1007 Lausanne, Switzerland*

## Synopsis

The sensitivity to radiation of mixtures of poly(methyl methacrylate) (PMMA) and polystyrene-co-acrylonitrile (SAN) was studied over the entire range of composition. Polystyrene-co-acrylonitrile, like polystyrene, is highly resistant to ionizing radiation, having a small  $G_x$  value for crosslinking (0.077) and an even smaller  $G_s$  value for main chain scission (0.055). In contrast, PMMA degrades readily under irradiation (with  $G_s = 1.2$ ). In  $\gamma$ -irradiated blends, the behavior of each polymer is largely influenced by the presence of the other component. Gel formation in SAN is impeded by PMMA, as a result of a decrease in  $G_x$ , and a concomitant increase in the ratio  $G_s/G_x$ . Flexural strength measurements, along with molecular weight determinations by gel permeation chromatography, demonstrated that SAN had a marked protective effect on PMMA by decreasing  $G_s$  (chain scission). This protective effect was not observed in earlier experiments with PMMA-PS blends, in spite of its chemical similarity to the system PMMA-SAN. The difference in behavior between PMMA-PS and PMMA-SAN may be explained on the basis of polymer compatibility. PMMA and SAN form a compatible pair, whereas PMMA and PS are incompatible; thus the short range protective effect of the phenyl groups in PS is inhibited.

## INTRODUCTION

Since the pioneering works of Charlesby<sup>1</sup> and Bopp and Sisman,<sup>2</sup> the effects of high energy radiation on a wide variety of homopolymers and some copolymers have been studied. A review was presented recently.<sup>3</sup> Essentially two phenomena occur for a given polymer under irradiation: crosslinking with an increase in molecular weight until the ultimate formation of a three dimensional network or main chain scission at random resulting in a decrease in molecular weight. In general both reactions occur simultaneously at different rates, depending on the chemical and physical nature of the polymer. Chemical groups differ widely in their sensitivity to radiation. The phenyl group in polystyrene and in aromatic polyimides has the highest known resistance,<sup>4,5</sup> and the methacrylate and sulfone groups are the most readily degradable.<sup>6,7</sup> Efforts to obtain polymers with high radiation stability led several groups to study irradiation behavior of copolymers containing phenyl units attached to the backbone.<sup>8,9</sup> The observations of the protective effect of phenyl groups in blends with polystyrene were inconclusive, however, due to phase separation as a consequence of polymer incompatibility.<sup>10-12</sup> Only in one instance was the protective effect of the phenyl moiety clearly assigned.<sup>13</sup>

A previous investigation<sup>14</sup> showed that the copolymer styrene-acrylonitrile (SAN) with azeotropic composition behaves essentially like polystyrene under

$\gamma$ -irradiation, and compatible blends can be obtained with poly(methyl methacrylate) throughout the entire range of composition.<sup>15,16</sup> The marked contrast in irradiation behavior between SAN and PMMA makes them ideal candidates for the investigation of the protective effects of the phenyl group in miscible polymer blends.

## EXPERIMENTAL

**Materials.** Commercial granulates of SAN (Luran 368R from BASF) and PMMA (7H from Röhm AG) were used without any further treatment. The acrylonitrile content of SAN is 38 mol % as determined by elementary analysis, which corresponds to the azeotropic composition for this copolymer.<sup>17</sup> The PMMA 7H is a copolymer of methyl methacrylate with 5% of ethyl methacrylate to improve mechanical properties.

Molecular weight measurements in our laboratory on nonirradiated samples gave, for SAN  $\overline{M}_n = 100,000$  by osmometry,  $\overline{M}_v = 160,000$  by viscosimetry, and  $\overline{M}_w = 230,000$  by gel permeation chromatography. For PMMA 7H the  $\overline{M}_w$  determined by gel permeation chromatography is 110,000. The molecular weight distribution in both polymers is close to the most probable distribution with  $\overline{M}_w/\overline{M}_n = 1.9\text{--}2.0$ .

Polymer granulates are dissolved in dimethyl formamide with different proportions of SAN and PMMA. Films of 50  $\mu\text{m}$  thickness are then casted from solution and carefully dried in vacuum. Bar specimens ( $60 \times 10 \times 3 \text{ mm}^3$ ) are compression moulded from the film. This technique allowed the production of homogeneous transparent specimens. Attempts to mix the polymers by coprecipitation in methanol gave opaque samples, probably as a result of phase separation, which are unsuitable for the present studies.

**Irradiation.** Irradiation was carried out under vacuum in sealed Pyrex tubes, with a  $\text{Co}^{60}$  source (Gammacell 220) at a nominal dose rate of 0.30 Mrad/h. To inspect for the presence of post-irradiation effects, some samples were annealed for several days before measurements at a few degrees above the glass transition temperature. However, no noticeable difference with freshly irradiated samples could be detected.

**Infrared Spectroscopy.** Infrared absorption spectra were recorded on a Perkin-Elmer 580B equipped with the 5300 data station. The swollen polymer gel was squeezed between two disks of KBr, and the optical path was adjusted to 0.1 mm with a PTFE spacer.

**Gel Permeation Chromatography.** Gel permeation chromatography was performed on a Waters 150 C with a set of three  $\mu$ -Styragel columns ( $10^5 + 10^4 + 10^3 \text{ \AA}$ ) and equipped with a variable wavelength UV detector (Perkin-Elmer LC-75) in series with a differential refractometer.

Molecular weight standards for SAN are not commercially available, and the calibration curve was constructed with PS standards from Pressure Chemicals using the universal calibration.<sup>18</sup> Mark-Houwink coefficients for PS are given in the literature<sup>19</sup>; those for SAN are determined by viscosimetry and membrane osmometry on fractions of SAN following a procedure recently described.<sup>20</sup>

**Sol-Gel Determination.** Sol and gel content of irradiated polymers are obtained by Soxhlet extraction with dichloromethane. Constant weight of the sol fraction is usually reached after 1 week. As a check for material balance, the

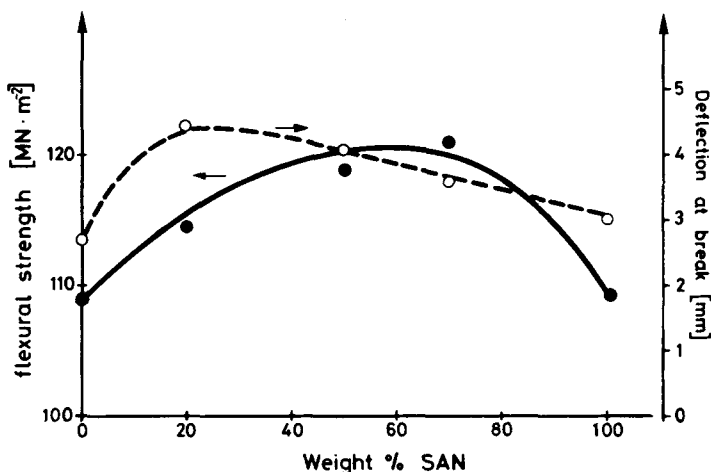


Fig. 1. Flexural strengths [(●) left scale] and deflection at break [(○) right scale] of unirradiated blends of PMMA and SAN, as a function of composition.

sol and gel parts are weighed separately and then compared with the original weight of the sample.

**Flexural Strength Measurements.** Three-point flexural strength measurements were carried out on an Instron universal tensometer (Model 1122) using a 40 mm span and a crosshead speed of 1 mm/min.<sup>21</sup> The flexural strength at break is given by<sup>21</sup>

$$\sigma = \frac{3}{2} P(L/bd^2)[1 + 6(D/L)^2 - 4(d/L)(D/L)]$$

with  $P$  = load at break,  $D$  = displacement of the center at break,  $L$  = span length,  $b$  = width of the specimen, and  $d$  = thickness of the specimen.

## RESULTS AND DISCUSSION

**Flexural Strength Tests.** Results of the flexural tests are given in Figures 1 and 2. Figure 1 shows the composition dependence of the flexural strength at break,  $\sigma_0$ , in nonirradiated blends of SAN and PMMA. In contrast to incompatible blends of PS and PMMA, flexural strength in the system SAN-PMMA goes through a maximum near the 50% by weight mixture which is similar to the curve obtained with the copolymer PS-co-PMMA.<sup>22</sup>

Dose dependence of flexural strength is presented in Figure 2. It is known that within a certain range of molar masses, flexural strength, and tensile-breaking stress depend linearly on molecular weight.<sup>23,24</sup> Using this property, it is possible to determine the rate of degradation under irradiation by measuring the initial rate of decrease in flexural strength as a function of dose.<sup>12,25</sup> From the results in Figure 3, it can be readily concluded that adding as little as 20% by weight of SAN to PMMA reduces the degradation effect of irradiation by a factor of 4. This inhibition effect is too important to be accounted for by a sole dilution effect not involving any protective mechanism of SAN upon PMMA.

**Molecular Weight Measurements.** Due to the approximate nature of the linear relationship between molar mass and flexural strength, particularly in

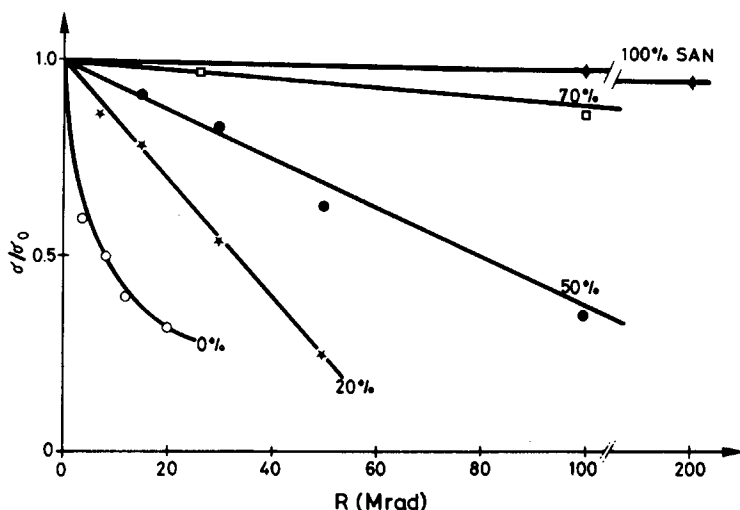


Fig. 2. Effects of irradiation dose and composition on the relative flexural strengths of PMMA-SAN blends. Each point represents the average of four to five measurements.

blends, mechanical tests can give only the trend in molecular weight changes. A more accurate method of molecular weight determination is necessary to ascertain the mechanism of protection, and this is provided by gel permeation chromatography. PMMA and SAN have different UV absorption spectra. By tuning the UV detector to two distinctly selected wavelengths, e.g., 260 nm and 232 nm for the present system, it should be possible in principle, to measure separately each component in the mixture.<sup>26</sup> In nonirradiated samples, the ratio of absorbance at 232 nm of PMMA to SAN is 4.76 in  $\text{CH}_2\text{Cl}_2$  at 30°C, and this ratio is equal to 0 at 260 nm. Unfortunately, the ratio of absorbances at 232 nm is not constant but increases with the irradiation dose due to a broadening of the absorption peak of SAN, thus adding uncertainties to the results. For the sake of precision, the two components of the blends were separated by fractionation prior to GPC measurements. After several investigations, it was found that a mixed solvent containing 90%  $\text{CH}_3\text{CN}$  + 10%  $\text{H}_2\text{O}$  by volume provided a convenient medium for the separation. At 60°C, both SAN and PMMA are soluble in pure  $\text{CH}_3\text{CN}$ . Adding 10%  $\text{H}_2\text{O}$  and cooling down to room temperature precipitated quantitatively the SAN. Each separated component is then dried in vacuum and weighed to control for material balance. Completeness of the separation is again checked with infrared spectroscopy.

In irradiated blends, quantitative recovery of PMMA became more and more difficult with the irradiation dose and percentage of SAN. Several extractions with  $\text{CH}_3\text{CN}$  containing a decreasing amount of  $\text{H}_2\text{O}$  were necessary.

Since PMMA and SAN behave completely differently, the radiation effects on the two components in the blend will be discussed in separate sections.

**Effect of Radiation on PMMA.** Gamma-radiolysis of pure PMMA is well understood, and a large amount of literature is already available.<sup>22-24</sup> PMMA belongs to the group of polymers disubstituted in the  $\alpha$ -position, and it gives under irradiation random main-chain scission without crosslinking.<sup>27,28</sup> It is expected that this behavior is preserved in blends.

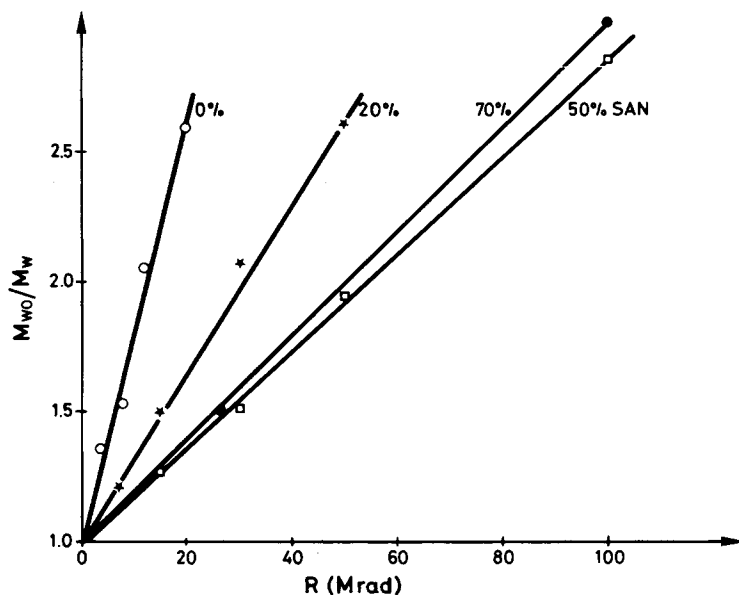


Fig. 3. Relative decrease in molecular weights of PMMA as a function of dose and composition in PMMA-SAN blends (initial weight-average molecular weight of PMMA is 110,000).

For a polymer with an initially most probable molecular weight distribution and which degrades exclusively by random main chain scission, the change in molar mass can be readily calculated using either eq. (1) or (2)<sup>29</sup>:

$$\frac{1}{\overline{M}_n} = \frac{1}{\overline{M}_{n0}} + \frac{G_s \cdot R}{0.96 \times 10^6} \quad (1)$$

$$\frac{1}{\overline{M}_w} = \frac{1}{\overline{M}_{w0}} + \frac{G_s \cdot R}{1.92 \times 10^6} \quad (2)$$

The subscript 0 refers to the molecular weights before irradiation,  $R$  is the absorbed dose in Mrad, and  $G_s$  the radiolytic yield for main-chain scission.

Either of the eq. (1) or (2) could be used to determine  $G_s$  from the slope of a plot of  $\overline{M}_{n0}/\overline{M}_n$  or  $\overline{M}_{w0}/\overline{M}_w$  as a function of dose. In practice,  $\overline{M}_n$  obtained from GPC is more prone to systematic and stochastic errors (noise, baseline drift) than  $\overline{M}_w$ , and eq. (2) will be preferred.

Gel permeation chromatography results for the PMMA fractions are shown in Figure 3. In mixtures, it is generally accepted that the deposition of energy

TABLE I  
Radiation Yields and Gelation Doses for  $\gamma$ -Irradiated PMMA-SAN Blends

% Weight SAN	10	20	50	70	100
$G_s$ (PMMA)	1.2	0.50	0.27	0.30	—
$G_s$ (SAN)	—	—	0.051	0.062	0.055
$G_x$ (SAN) <sup>a</sup>	—	—	0.025	0.043	0.077
$G_s/2G_x$	—	—	1.0	0.72	0.36
$R_{gel}$ (Mrad)	—	—	198	87	38

<sup>a</sup> Calculated from the gel dose using (31):  $R_{gel}$  (Mrad) =  $(1.92 \times 10^6)/(4G_x - G_s)\overline{M}_w$

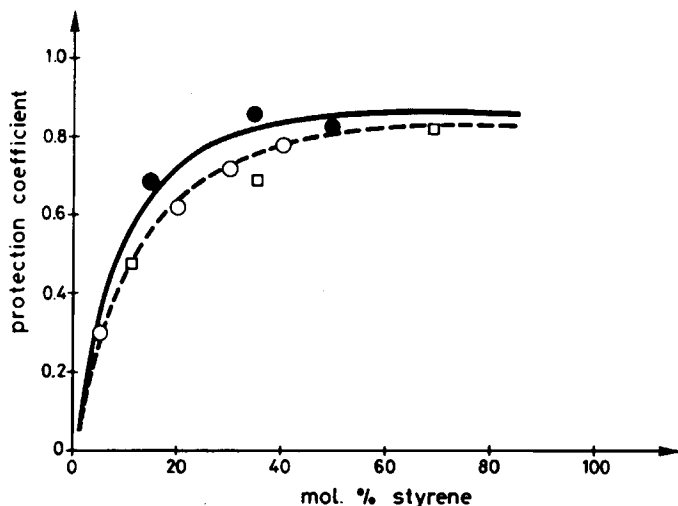


Fig. 4. Variation of the protection coefficient with concentration of styrene units in copolymers and blends: (O) poly(dimethyl-diphenyl-co-disiloxane) (Ref. 13); (□) poly(isobutylene-co-styrene) (Ref. 8); (●) poly(methyl methacrylate) + poly(styrene-co-acrylonitrile) blends (this work).

during the physical stage, is distributed indiscriminately among the components, in proportion to their electron density.<sup>30</sup> The radiolytic yields for main-chain scission in PMMA,  $G_s$  (PMMA), corrected for the small difference in fractional electron density in the blend, are reported in Table I. In pure PMMA, the value of 1.2 found for  $G_s$  is in complete agreement with previous results.<sup>31,32</sup>

If there were no influence of SAN on PMMA,  $G_s$  (PMMA) should remain constant and independent of composition. The observed decrease of  $G_s$  (PMMA) with the percentage of SAN is indicative of a protection effect of the latter component. The apparent increase in  $G_s$  (PMMA) in the 70% blends as compared to the same quantity at 50% SAN is within the 10% limit of precision of the measurements. Such an inversion may be expected, however, because of a grafting reaction (see below), which tends to deplete selectively high molecular weight molecules.

Let us call  $R_{1/2}$  and  $R'_{1/2}$  the radiation doses needed to reduce the molecular weight of PMMA by one half, in the absence and in the presence of SAN respectively. The protection efficiency of SAN can be expressed by the protection coefficient  $p$  defined as  $1 - (R_{1/2}/R'_{1/2})$ .<sup>13</sup> The resulting plot in Figure 4 indicates that the protection coefficient initially increases rapidly with the concentration of the phenyl group, and then levels off at about 40 mol % of styrene, to a limiting value of 0.85. Compared to results from other systems (Fig. 4), the protection efficiency of the phenyl group in SAN is slightly larger than in the copolymers dimethyl-diphenyl-co-disiloxane<sup>9,13</sup> or isobutylene-co-styrene.<sup>8</sup> At least one explanation may account for this higher protection effect: the cyano group in acrylonitrile can act as an electron scavenger,<sup>33</sup> adding this protective effect to the quenching capabilities of the phenyl group.

The internal protection effect of the phenyl group, in small alkane molecules<sup>34</sup> and in styrene copolymers<sup>8,9,13</sup> was found to extend over four to six neighboring units or about 0.6 nm. The similarity of our data with those obtained with copolymers suggested that the same range and the same mechanisms of protection

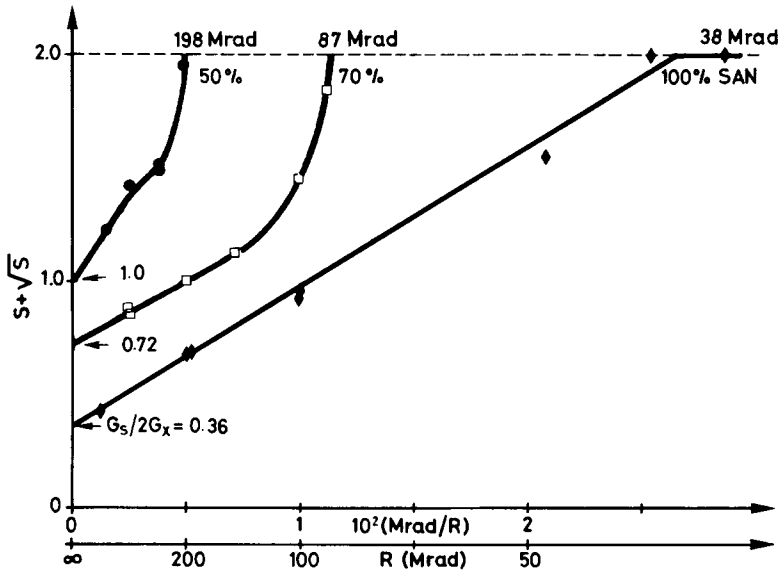


Fig. 5. Charlesby-Pinner plot of the sol fraction  $s$  for the SAN component. In irradiated blends of PMMA/SAN the quantity  $s$  is calculated according to the following equation:

$$s = \frac{\text{wt sol fraction of SAN} / \text{wt SAN in blend} = (\text{total wt sol} - \text{wt PMMA in blend} + \text{wt grafted PMMA}) / \text{wt SAN in blend.}}{}$$

should prevail in external protection as well. Only at the beginning does the protection coefficient increase linearly with the concentration of the protector. As soon as the protective spheres of the phenyl units start to overlap, at 15–20 mol % of styrene, the protection coefficient tends to level off and finally reaches a plateau, as observed in Figure 4. A similar residual degradation in copolymers had been explained in terms of the statistical distribution of monomer sequences.<sup>9</sup> In compatible blends, however, large fluctuations in concentration are very improbable, and this explanation cannot hold. It is more reasonable to assume that some excited states of the PMMA molecule are not quenched by the phenyl group and account for the remaining chain scission.

**Effects of Irradiation on the SAN Component.** In pure SAN, crosslinking and main-chain scission occur simultaneously<sup>14</sup> with  $G_x = 0.077$  and  $G_s = 0.055$ . Provided the initial molecular weight distribution follows a random distribution, the sol fraction  $s$  obeys the relationship<sup>29</sup>

$$s + \sqrt{s} = \frac{0.96 \times 10^6}{\overline{M_w} \cdot G_x} \cdot \frac{1}{R} + \frac{G_s}{2G_x}$$

The Charlesby-Pinner plot of  $s + \sqrt{s}$  as a function of  $1/R$  should give, in this case, a straight line with an origin intercept at  $G_s/2G_x$ . The incipient dose for gelation  $R_{\text{gel}}$  is determined from the sol curve at  $s + \sqrt{s} = 2$ .

In blends of SAN and PMMA, the sol fraction  $s$  can either be referred to the total weight of the sample, or to the SAN component alone. The second alternative seems to be more logical since only SAN crosslinks under irradiation. Furthermore, as will be seen below, a small fraction of PMMA is grafted onto the gel. The experimentally determined weight of the gel should be subtracted

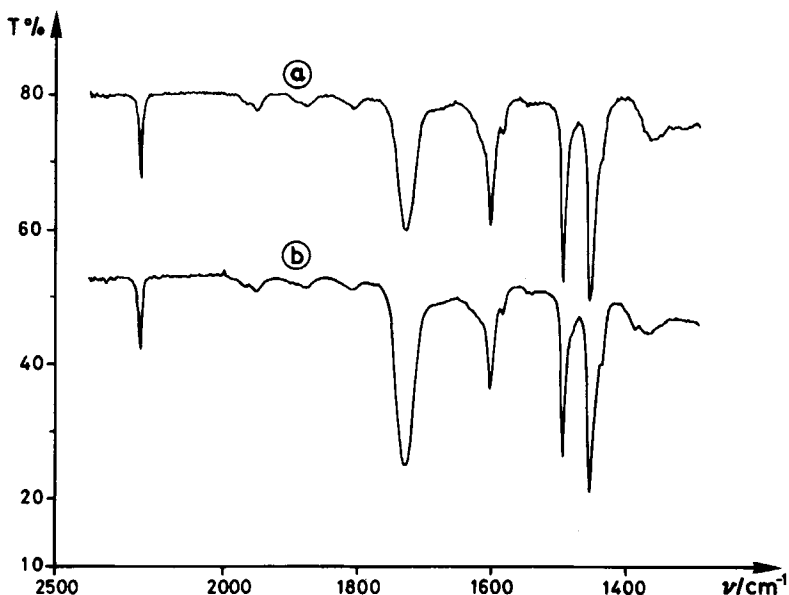


Fig. 6. Infrared absorption spectra of the extracted gel in irradiated blends of PMMA and SAN: (a) blend with 70% weight of SAN, irradiated for 200 Mrad; (b) blend with 50% weight of SAN, irradiated for 260 Mrad. For reasons of clarity, the ordinate of curve (b) is shifted downward by about 25%. The gels are swollen to equilibrium in  $\text{CHCl}_3$ ; the reported spectra are subtracted from the absorption of the solvent  $\text{CHCl}_3$ . The most characteristic absorption bands are at  $2240\text{ cm}^{-1}$  ( $-\text{C}\equiv\text{N}$  stretch of acrylonitrile) and  $1730\text{ cm}^{-1}$  ( $>\text{C}=\text{O}$  stretch of methyl methacrylate).

from this contribution. A plot with the sol fractions determined that way is shown in Figure 5.

In pure SAN, the slight departure of the plot from a straight line at low doses can originate in chemical heterogeneities in composition of the copolymer or in deviations from a random molecular weight distribution. In blends, the plot is definitely curved at any concentration of PMMA. The upward curvature of the sol curves probably originates from chemical interactions between the different components in the mixture. Some experiments are underway to corroborate this hypothesis. Quantitative evaluation of the chemical effects can be quite cumbersome however, since the molecular weight distribution of each component should be taken into account in the calculations.<sup>35</sup> Regardless of the shape of the curve, the intercept at the extrapolated infinite dose can be determined unambiguously to give the ratio  $G_s/2G_x$ . The different values for radiation yields are given in Table I.

**Grafting of PMMA on SAN.** When two polymer chains are in close contact, a grafting reaction can occur by recombination between macroradicals of PMMA and one of SAN. In order to detect an eventual grafting reaction between PMMA and SAN, narrow fractions of PMMA and SAN were blended and irradiated at doses less than the gel point. GPC measurements, performed on these blends failed to identify significant grafting between PMMA and SAN.

Infrared spectra of the insoluble fraction in irradiated blends showed, however, the presence of carbonyl groups which presumably come from PMMA incorporated into the network (Fig. 6).



Since under irradiation PMMA degrades exclusively, its presence in the gel can only be explained if a grafting reaction had occurred. The infrared absorption coefficient of the carbonyl group in PMMA is 18 times stronger than the absorption coefficient of the cyano group in SAN. Using this ratio, it was determined that the gel fraction of 70% SAN blends contained 8.6% by weight of grafted PMMA. This proportion increased to 13.8% in 50% SAN blends.

## CONCLUSION

Mechanical tests, molecular weight, and solubility measurements on irradiated PMMA-SAN blends show that phenyl substitution in one of the polymers can offer partial radiation protection to the other component. This effect is in many respects similar to the internal protection found in copolymers with styrene, suggesting that probably the same mechanisms are involved in both cases. Protective effects of the phenyl group are short-range and become effective only in compatible blends where mixing at the molecular level is possible. In systems where phase separation occurred, no such effect of the aromatic group could be observed. The protection is not complete, however, since some 15% of the initial yield for main-chain scission in PMMA could not be suppressed, even at high styrene concentration. This finding is in agreement with results obtained in styrene copolymers<sup>9,13</sup> and in mixtures of small organic substances containing benzene.<sup>36</sup>

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