

Effects of Nuclear Radiations on Structure and Molecular Motions in Some Crystalline Stereoregular Polymers*

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Synopsis

Young's modulus and the mechanical damping factor have been determined between -180 and $+280^{\circ}\text{C}$. (at a frequency of several kilocycles), in samples of isotactic polypropylene, isotactic polystyrene, and *trans*-1,4-polybutadiene, subjected to pile irradiation (γ -rays and neutrons) at γ -doses from 90 to 4000 Mrad. In isotactic polypropylene no important structural changes are produced by the irradiation, except for a partial destruction of crystallinity. The samples receiving high radiation doses exhibit a low temperature loss region, which is attributed to the formation of a certain number of branches. Isotactic polystyrene shows very slight modifications of the dynamic mechanical properties at room temperature. At low temperature an increase of intensity of the δ relaxation phenomenon (probably due to oscillations of phenyl rings) with increasing radiation dose is observed. Important structural modifications produced by the radiation, destruction of crystallinity accompanied by crosslinking, which transform the material into a crosslinked rubber, are observed in *trans*-1,4-polybutadiene. Unlike conventional (sulfur) vulcanization, crosslinking by radiation does not cause a marked shift of the glass transition point. A secondary low-temperature relaxation effect, not existing in the unirradiated material, appears in the mechanical loss curves of the irradiated samples; it is attributed to the formation of $-\text{CH}_2-$ sequences in the main chains through saturation of $\text{C}=\text{C}$ bonds. The mechanical spectrum of irradiated polybutadiene is very similar to those shown by crosslinked ethylene-butadiene copolymers.

The main effects caused by irradiation of high polymers with high-energy particles are the formation of crosslinks between macromolecular chains and degradation. Such transformations are usually accompanied by development of gaseous products (hydrogen, carbon monoxide, carbon dioxide, hydrocarbons, etc.) and, in the case of crystalline products, by partial or complete destruction of crystallinity.

The reactions which predominate and determine the final physical properties of the products irradiated depend in part on the chemical structure and physical state of the polymer subjected to irradiation, in part to the stability of the free radicals formed during such treatment. In the case of vinyl polymers it has been found that a certain relationship

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exists between chemical structure and irradiation effects, so these materials can be classified into network-forming and degrading polymers. Polyethylene, for example, belongs to the first category and tends on irradiation to be transformed to highly crosslinked products; polyisobutylene, on the contrary, belongs to the second category and, under the action of the radiations, degrades.

In a series of investigations on the effects of irradiation on physical properties of high polymers carried out recently in our laboratories, the dynamic mechanical properties (Young's modulus and damping factor) of some stereoregular crystalline polymers (isotactic polypropylene, isotactic polystyrene, and *trans*-1,4-polybutadiene), irradiated in the atomic pile, have been determined.

As Young's modulus and mechanical losses are strictly related to the structure, to the types of forces existing between macromolecules, and to their molecular mobility, the investigation of the dynamic mechanical properties at different temperatures can give very useful information about changes provoked by irradiation in high polymers.

Of the polymers examined, polypropylene, whose chemical structure is intermediate between that of polyethylene and that of polyisobutylene, degrades and crosslinks simultaneously.¹⁻³

Polystyrene, on the contrary, practically does not degrade at all, but shows a certain limited tendency to crosslinking, specially when high doses of radiation are employed.^{4,5} The high radiation resistance exhibited by this polymer has been attributed to the protective action exerted by the presence of the bulky phenyl rings along the chain.⁶ Consequently, the radiation effects on polystyrene may be regarded, at least from certain points of view, beneficial rather than deleterious, considering that the formation of crosslinks improves the resistance of the material both to solvent attack and to the action of heat.

Polybutadiene behaves in a similar way to diene elastomers and natural rubber.⁷⁻¹⁰ It exhibits, in fact, a very peculiar tendency for crosslinking without showing, at least for not too large doses of radiation, degradation effects. The radiochemical yield for crosslinking G_x is particularly high and increases with increasing dose if irradiation is carried out at temperatures above the glass transition point (-80°C). During irradiation a certain quantity of gases (hydrogen, methane, ethylene, propane, etc.) is evolved. The quantity of hydrogen evolved is much lower than the theoretical amount calculated on the basis of liberation of two hydrogen atoms for each C—C crosslink formed; this discrepancy has been explained by supposing that most of the hydrogen liberated during irradiation is to be utilized to lower the degree of unsaturation of the macromolecular chains.¹⁰

Also *cis-trans* isomerization occurs in irradiated polybutadiene; particularly, when polymers with prevailing *cis*-1,4-structure are irradiated.¹¹ In the case of *trans*-1,4-polybutadiene, however, the isomerization reaction very soon reaches an equilibrium state corresponding to about 80% of the total insaturation.^{12,13}

EXPERIMENTAL

Samples of isotactic polypropylene and polystyrene and of *trans*-1,4-polybutadiene have been examined.

All samples subjected to irradiation were compression-molded in an inert (nitrogen) atmosphere, in the form of small cylinders (0.8 cm. diameter, 6 cm. height), then annealed for about 48 hr. (in presence of nitrogen) at temperatures about 10°C. below the relative melting point, and finally slowly cooled to room temperature.

The irradiation was executed in the reactor of the Sorin Society in Saluggia (Italy) with mixed radiations (fast and slow neutrons and associated radiations) at room temperature, in presence of air, with gamma doses (absorbed) varying from 90 to 4000 Mrad.

The presence of oxygen may profoundly modify the mechanism of reactions occurring in high polymers in the course of irradiation; however substantial differences between samples irradiated *in vacuo* and samples irradiated in the presence of air, have only been found for specimens in the form of very thin sheets. In our case, owing to the relatively large dimensions of the specimens submitted to irradiation and to the low permeability towards oxygen shown by the materials examined, the effects of the irradiation in air are practically equivalent to those obtainable under vacuum.

Of the various samples, after irradiation, the dynamic mechanical properties (dynamic Young's modulus E and damping factor Q^{-1}) were determined by an electrostatic method at medium frequency (several kilocycles) based on the excitation of extensional vibrations of the specimen, in a temperature range from -180 to 240°C. Young's modulus E was calculated from the measured fundamental resonance frequency f by means of the simplified equation:

$$E = 4f^2l^2d = dv^2$$

where d is the density, l the length, and v the sound velocity of the specimen.

As measure of the damping factor the reciprocal of the resonance coefficient Q was taken, the latter being calculated from the width of the resonance curve. All the measurements were carried out under vacuum, with a residual pressure of about 10^{-3} mm. Hg, in order both to reduce additional energy dissipation due to the air viscosity and to avoid temperature variations during the execution of the experimental measurements.

RESULTS

Isotactic Polypropylene

Eight samples of isotactic polypropylene (intrinsic viscosity $[\eta] = 3.26$ dl./g. in decalin at 135°C., $d_{20} = 0.914$ g./cm.³, x-ray crystallinity 75%, melting point $T_m = 174^\circ\text{C}$.), commercial products of Montecatini S.p.A., irradiated with doses varying from 90 to 2200 Mrad (gamma doses absorbed), with integrated flux between 0.19 and 39.90×10^{16} thermal neutrons/cm.², have been examined.

In Table I the experimental values of the density d , sound velocity v , Young's modulus E , and damping factor Q^{-1} determined at 20°C. are reported as functions of the radiation dose adsorbed R and of the integrated thermal neutron flux Φ .

In Figure 1 the values of the density and of the Young's modulus are shown graphically as functions of the radiation dose R .

As it can be seen from the data reported in Table I and Figure 1, the density, in the early stages of the irradiation (for doses up to 270 Mrad) remains constant, then for higher doses tends to decrease, passes through a minimum value (for $R = 1320$ Mrad), and finally increases with increasing radiation dose. The Young's modulus decreases in the early stages of irradiation, passes through a minimum value for $R = 1320$ Mrad, and finally increases with increase of the radiation dose adsorbed.

TABLE I
Density, Sound Velocity, Young's Modulus, and Damping Factor at 20°C.
in Irradiated Isotactic Polypropylene

Sample	R , Mrad	$\Phi \times 10^{-16}$, thermal neutrons/ cm. ²	d , g./cm. ³	v m./sec.	$E \times$ 10^{-10} dyne/ cm. ²	$Q^{-1} \times 10^2$
1	—	—	0.914	2200	4.47	7.60
2	90	0.190	0.914	2170	4.34	9.00
3	180	0.965	0.914	1860	3.16	11.00
4	270	1.450	0.914	1600	2.34	13.80
5	360	1.930	0.911	1500	2.05	12.00
6	860	9.780	0.894	1400	1.75	11.40
7	1320	23.700	0.889	1300	1.50	21.00
8	1800	18.300	0.893	1500	2.01	19.10
9	2200	39.900	0.895	1550	2.10	7.00

In Figures 2-4 the value of Young's modulus and of the damping factor, relative to the different specimens irradiated with different doses, are reported as functions of temperature from about -180° to 180°C .

The Young's modulus of the unirradiated sample at temperatures below T_g assumes values of the order of 8×10^{10} dyne/cm.², characteristic of rigid polymers; with increasing temperature, it first decreases slightly, due to the thermal expansion, and then, between T_a (-10°C .) and T_s (60°C .) exhibits a sharp drop of values due to the excitation of cooperative motions in the main chain (glass transition) (Fig. 2).¹⁴ At higher temperatures, E still continues to decrease with increasing T but at a rate comparable with that shown in the low-temperature range.

Behavior analogous to that described above is shown by the E - T curves for specimens subjected to irradiation; the only differences which can be noted as compared with the unirradiated sample consist simply in changes in the absolute values of Young's modulus and in the position of T_g , which shows a small shift towards lower temperatures.

In the unirradiated sample the damping factor Q^{-1} at temperatures below T_g , is characterized by relatively low values (of the order of 1×10^{-2}); at higher temperatures, it tends initially to increase and then to decrease after having passed through a maximum value T_d at about 40°C . (Fig. 2).

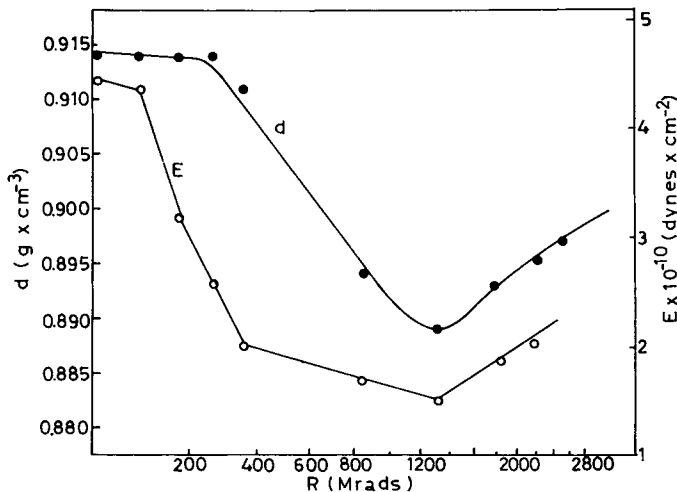


Fig. 1. Density d and Young's modulus E at 20°C . in isotactic polypropylene irradiated with doses up to 2200 Mrad as functions of radiation dose.

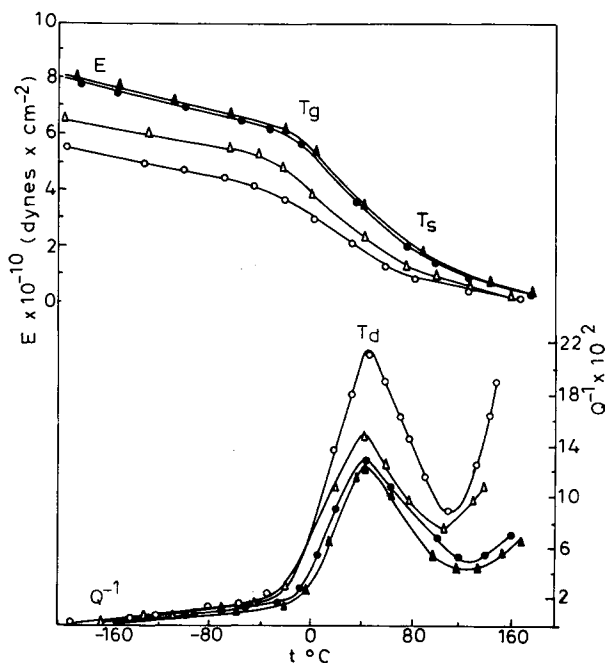


Fig. 2. Young's modulus E and the damping factor Q^{-1} as functions of temperature in isotactic polypropylene irradiated with doses up to 270 Mrad: (▲) unirradiated; (●) $R = 90$ Mrad; (△) $R = 180$ Mrad; (○) $R = 270$ Mrad.

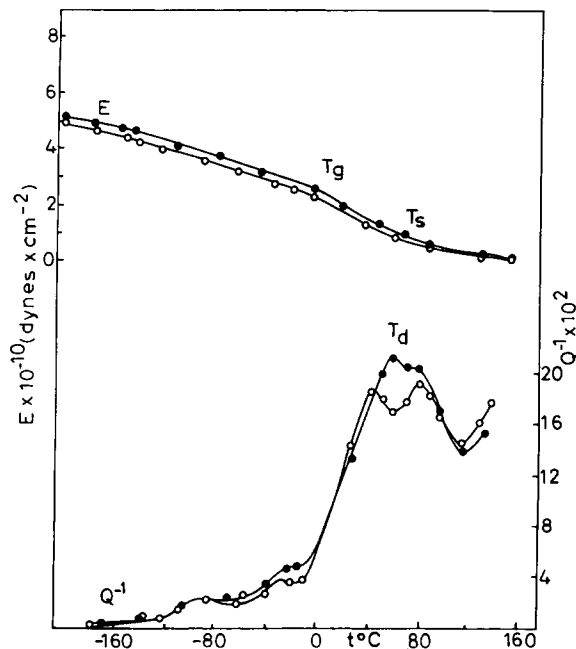


Fig. 3. Young's modulus E and the damping factor Q^{-1} in isotactic polypropylene irradiated with (●) 360 Mrad and (○) 860 Mrad, as functions of temperature.

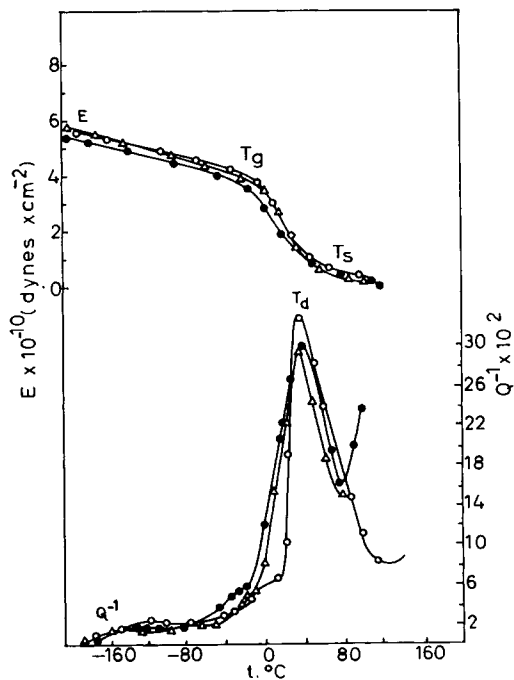


Fig. 4. Young's modulus E and the damping factor Q^{-1} in isotactic polypropylene irradiated with (●) 1320 Mrad, (○) 1800 Mrad, and (△) 2200 Mrad as functions of temperature.

The existence of a maximum of mechanical loss at 40°C. is attributed to the relaxation effect associated with the glass transition.¹⁴

Analogous behavior is also shown by the samples irradiated with doses up to 270 Mrad; however, the damping peak, although it remains practically fixed on the temperature scale, shows a progressive increase of height with increasing radiation dose (Fig. 2).

The samples subjected to higher radiation doses exhibit a behavior similar to that of the unirradiated sample, except for secondary relaxation effects at low temperature, characterized by a high loss region extending from about -100 to about -40°C. which does not appear in the mechanical loss curves of the preceding samples (Figs. 3 and 4). Besides for the sample irradiated with $R = 860$ Mrad the peak in the $Q^{-1}-T$ curve is separated into two peaks close to each other.

Isotactic Polystyrene

The isotactic polystyrene samples subjected to irradiation had the following characteristics: $[\eta] = 2.19$ dl./g. (in benzene at 30°C.); $d_{20} = 1.08$ g./cm.³, x-ray crystallinity about 40%, $T_m = 230^\circ\text{C}$.). The material was furnished by Montecatini S.p.A.

In Table II values of the density d , the sound velocity v , the Young's modulus E , and the damping factor Q^{-1} determined at 20°C. in six samples of isotactic polystyrene, receiving irradiation doses R of 90-3600 Mrad, with integrated flux Φ between 0.189 and 64.7×10^{16} thermal neutrons/cm.² are reported.

As can be seen from the data reported in Table II, in the samples submitted to irradiation, while the density and the damping factor remain constant, the sound velocity and Young's modulus exhibit gradual slight decreases with increasing radiation dose.

In Figure 5 the values of the Young's modulus and of the damping factor of the unirradiated sample and of the samples irradiated with relatively low doses (up to 360 Mrad) are reported as functions of temperature between room temperature and the melting point.

TABLE II
Density, Sound Velocity, Young's Modulus, and Damping Factor at 20°C. in
Irradiated Isotactic Polystyrene

Sample	R , Mrad	$\Phi \times 10^{-16}$ thermal neutrons/ cm. ²	d , g./cm. ³	v , m./sec.	$E \times$ 10^{-10} , dyne/ cm. ²	$Q^{-1} \times$ 10^2
1	—	—	1.08	2300	5.72	1.0
2	97	0.189	1.08	2280	5.62	1.0
3	360	3.740	1.08	2260	5.52	1.0
4	680	6.910	1.08	2225	5.35	1.0
5	1320	23.700	1.08	2160	5.03	1.0
6	3600	64.700	1.08	2130	4.00	1.0

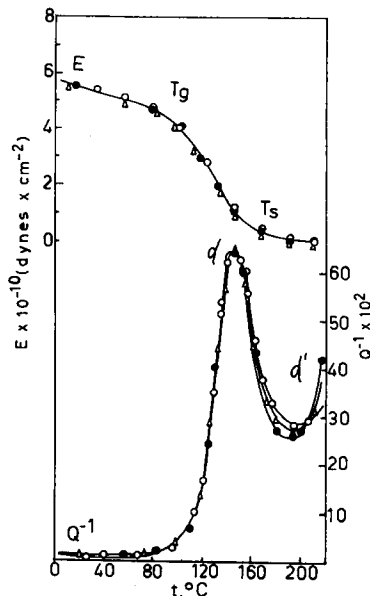


Fig. 5. Young's modulus E and the damping factor Q^{-1} in isotactic polystyrene irradiated with doses up to 360 Mrad as functions of temperature between room temperature and the melting point: (O) unirradiated; (●) $R = 97$ Mrad; (Δ) $R = 360$ Mrad.

In the unirradiated sample it can be observed, starting from room temperature, that the Young's modulus, with increasing temperature, at first remains practically constant, showing only a slight decrease of values due to the thermal expansion; successively, between T_g ($100^\circ\text{C}.$) and T_s ($160^\circ\text{C}.$) exhibits a marked drop of values, due to the glass transition.¹⁴ At still higher temperatures, the E - T curve shows a behavior which is quite similar to that shown in the lower temperature (below T_g) range till the melting point is reached.

The damping factor curve at temperatures below T_g shows relatively low mechanical loss values which are practically constant with increasing temperature. At temperatures above the glass transition point T_g , two high-loss regions are seen: one, α , characterized by a rather sharp maximum of damping at about $140^\circ\text{C}.$ and another, α' , which begins at temperature a little below $200^\circ\text{C}.$, characterized by a rapid increase of mechanical loss with increasing T .

The elastic and anelastic behavior of the samples submitted to low radiation doses, in the temperature range considered, is quite similar to that shown by the unirradiated sample: no significant difference is found, even between the absolute values of the quantities measured.

In Figure 6 the Young's modulus and damping factor values determined between room temperature and $240^\circ\text{C}.$ for isotactic polystyrene samples subjected to higher radiation doses (680–3600 Mrad) are plotted against temperature. For these samples, with increasing radiation doses, a pro-

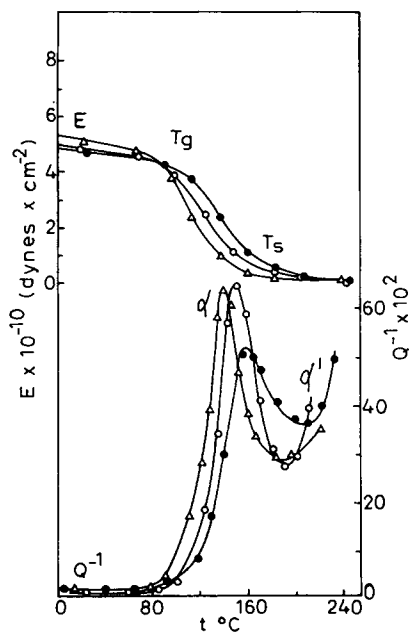


Fig. 6. Young's modulus E and the damping factor Q^{-1} in isotactic polystyrene irradiated with (Δ) 680 Mrad, (\circ) 1320 Mrad and (\bullet) 3600 Mrad as functions of temperature between room temperature and the melting point.

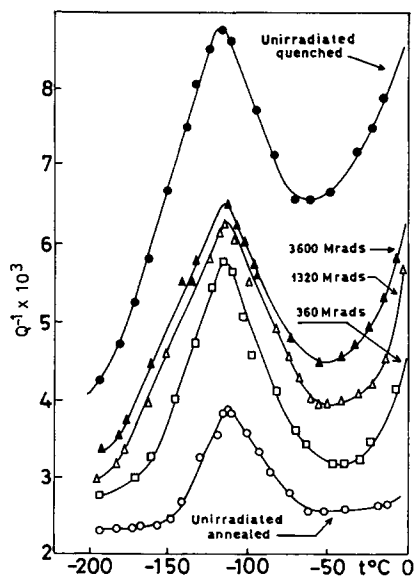


Fig. 7. Damping factor in irradiated isotactic polystyrene as function of temperature in the low temperature range.

gressive small shift of the glass transition point T_g and of the α damping peak towards higher temperatures is observed.

In Figure 7 the values of the damping factor for the low-temperature range (between room temperature and $-180^\circ\text{C}.$) are reported against temperature for some of the isotactic polystyrene samples examined, together with the corresponding curves for two unirradiated samples, under annealed and quenched (amorphous) conditions. Quenching was carried out by dropping a sample of molten, unirradiated isotactic polystyrene into liquid nitrogen.

As the experimental data reported in Figure 7 indicate, at very low temperature, in isotactic polystyrene another loss peak exists, which has been attributed to a secondary relaxation effect (δ transition), probably associated with oscillations or wagging of phenyl rings around the C—C bond, which link them to the main chain. The activation energy of this process, calculated from the shift of the loss peak temperature with frequency, is about 9.0 kcal./mole.¹⁵

Comparing the experimental results for irradiated samples with those of the unirradiated, annealed polymer shows that, with increasing radiation dose, while the position of the δ peak on the temperature scale remains practically unchanged, its height tends to increase.

The maximum height for the δ peak is exhibited by the unirradiated quenched sample (amorphous).

trans-1,4-Polybutadiene

The polybutadiene samples subjected to irradiation, commercial product (Phillips), had the following characteristics: $[\eta] = 1.26$ dl./g. (in benzene at $25^\circ\text{C}.$), $d_{20} = 0.972$ g./cm.³, x-ray crystallinity $\simeq 40\%$; $T_m = 90^\circ\text{C}.$; composition 90% *trans*-1,4; 8% *cis*-1,4; 2% 1,2).

In Table III the experimental density d , sound velocity v , Young's modulus E , and damping factor Q^{-1} , determined at $20^\circ\text{C}.$ are reported

TABLE III
Density, Sound Velocity, Young's Modulus, and Damping Factor at $20^\circ\text{C}.$ in
Irradiated *trans*-1,4-Polybutadiene

Sample	R , Mrad	$\Phi \times$ 10^{-16} , thermal neutrons/ cm. ²	d , g./cm. ³	v , m./sec.	$E \times$ 10^{-10} , dyne/ cm. ²	$Q^{-1} \times 10^2$
1	—	—	0.972	700	0.476	5.20
2	200	1.8	0.950	400	0.152	5.80
3	400	5.0	0.940	380	0.136	7.35
4	600	9.3	0.950	470	0.210	10.50
5	1500	16.0	0.970	800	0.621	15.35
6	2000	35.0	0.972	950	0.879	10.50
7	4000	71.8	0.995	1230	1.500	4.30

for seven samples of *trans*-1,4-polybutadiene, irradiated with doses varying from 200 to 4000 Mrad, with integrated flux between 1.8 and 71.8 thermal neutrons/cm.²

In Figure 8 the density and the Young's modulus values at 20°C. are plotted against radiation dose *R*.

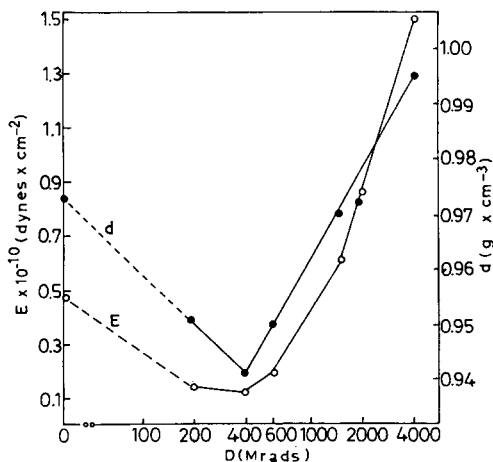


Fig. 8. Density *d* and Young's modulus *E* at 20°C. in *trans*-1,4-polybutadiene irradiated with doses up to 4000 Mrad as functions of radiation dose.

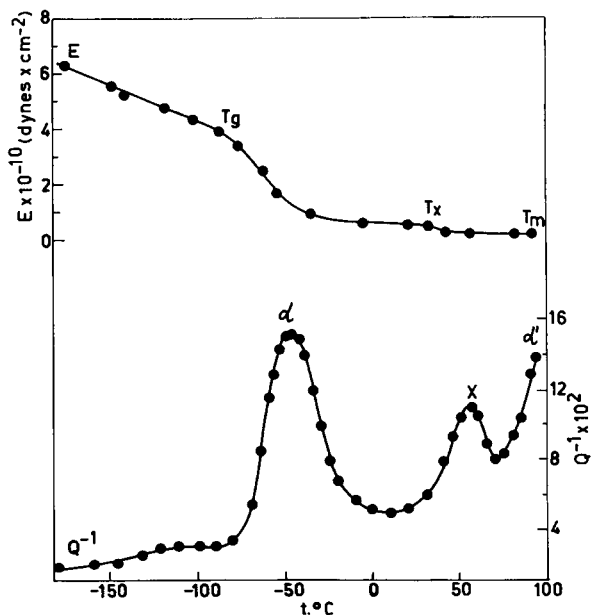


Fig. 9 Young's modulus *E* and damping factor *Q*⁻¹ in *trans*-1,4-polybutadiene as functions of temperature.

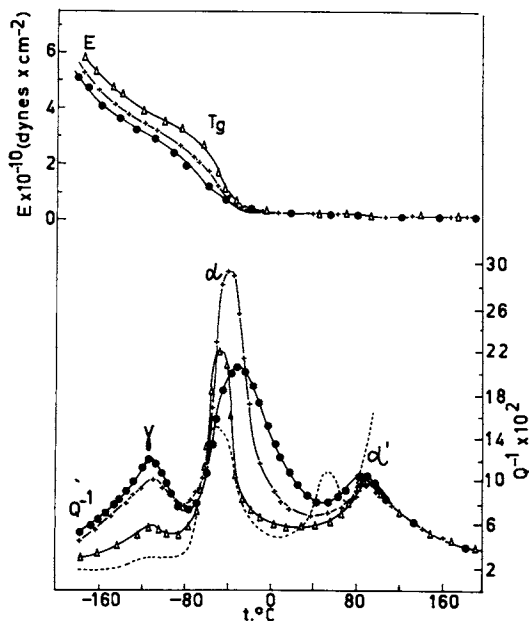


Fig. 10. Young's modulus E and damping factor Q^{-1} in *trans*-1,4-polybutadiene samples irradiated with doses up to 600 Mrad as functions of temperature: (Δ) $R = 200$ Mrad; (+) $R = 400$ Mrad; (\bullet) $R = 600$ Mrad.

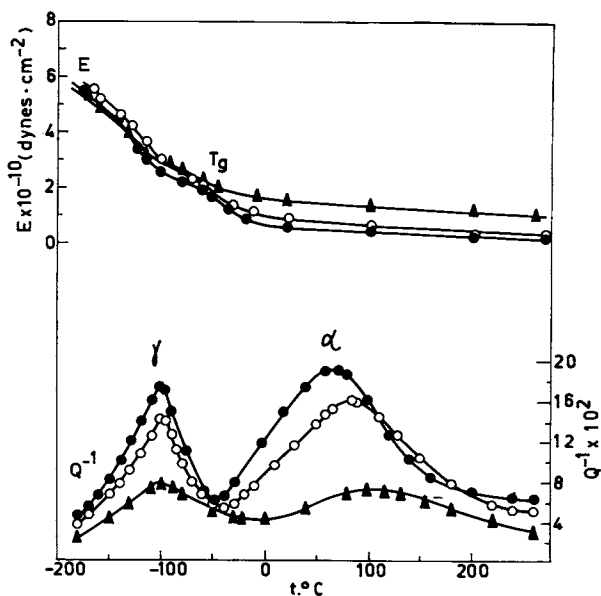


Fig. 11. Young's modulus and damping factor in *trans*-1,4-polybutadiene samples irradiated with doses between 500 and 4000 Mrad as functions of temperature (\bullet) $R = 1500$ Mrad; (\circ) $R = 2000$ Mrad; (\blacktriangle) $R = 4000$ Mrad.

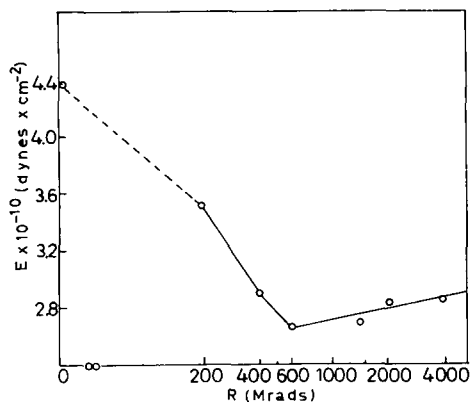


Fig. 12. Young's modulus at -100°C . of irradiated *trans*-1,4-polybutadiene as function of radiation dose.

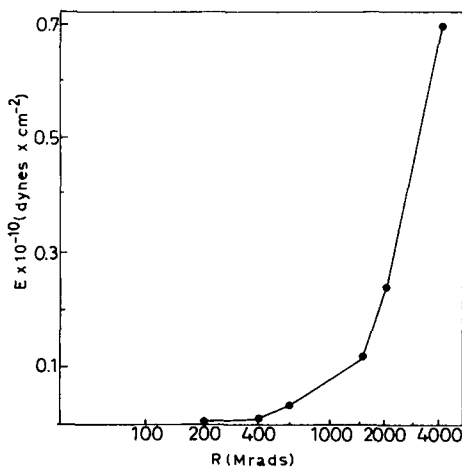


Fig. 13. Young's modulus at 160°C . in irradiated *trans*-1,4-polybutadiene as function of radiation dose.

The data reported in Table III and Figure 8, show that, with increasing radiation dose adsorbed, the density and the Young's modulus first tend to decrease, reach minimum values for $R = 400$ Mrad, and finally increase. The damping factor, on the contrary, tends first to increase with increasing radiation dose and then for higher radiation doses, decreases, after passing through a maximum value at 1500 Mrads.

In Figure 9 the Young's modulus and the damping factor of the un-irradiated sample at different temperatures between -180 and $+100^{\circ}\text{C}$., are reported as functions of T . The $E-T$ curve exhibits three successive changes of slope at about -75°C . (T_g), $+30^{\circ}\text{C}$. (T_x) and $+90^{\circ}\text{C}$. (T_m), attributed respectively to the excitation of cooperative motions of chain segments in the amorphous regions (glass transition), to a crystalline phase transition, and to the melting of crystalline regions.¹⁶

The Q^{-1} - T curve for the same unirradiated sample exhibits two mechanical loss maxima, one (α) located at -48°C . and another (X) at $+55^{\circ}\text{C}$., and a high dissipation region (α'), near the melting point of the material, characterized by a rapid increase of mechanical loss with increasing temperature. The three phenomena are associated with the corresponding transitions of the modulus, which occur in the same temperature range as above indicated.

In Figures 10 and 11, Young's modulus and damping factor determined in the samples of irradiated *trans*-1,4-polybutadiene are reported as functions of temperature between -180 and 240°C .

From the comparison of the Young's modulus and damping factor versus temperature curves, for the irradiated and unirradiated samples, the following main differences can be observed.

(1) At low temperature, below T_g , with increasing radiation dose, E first decreases, then reaches a minimum value between 600 and 1500 Mrad, and finally shows a small increase (Fig. 12). At temperatures above the crystalline melting point, while the Young's modulus of the unirradiated sample drops to very low values, due to the viscous flow, the modulus of the irradiated samples assumes values of the order of 10^8 dyne/cm.², characteristic of rubbery materials, whose values increase with increasing radiation dose and with increasing temperature (Fig. 13).

(2) The crystalline phase transition, which occurs at T_x in the unirradiated sample, is not noted in unirradiated samples after the early stages of irradiation (Fig. 10).

(3) The position of the glass transition point, on the temperature scale, remains practically unchanged after irradiation, despite the increase of the network density (Figs. 10 and 11).

(4) In all the irradiated samples a new secondary relaxation effect (γ) is observed at low temperature, characterized by a damping maximum at about -100°C . (Figs. 10 and 11). The position of the damping peak on the temperature scale is practically the same for all the samples; the height of the γ peak on the other hand, first increases with increasing radiation dose and then tends to decrease, after passing through a maximum.

(5) The main damping peak (associated with cooperative motions in the main chain) is shifted towards higher temperatures with increasing radiation dose. Its height first increases and then decreases with increasing R , after passing through a maximum at $R = 400$ Mrad (Figs. 10 and 11).

DISCUSSION OF RESULTS

The examination of the experimental results permits first of all confirmation of the differences in behavior of the different materials investigated.

Polypropylene

The effects of the irradiation on isotactic polypropylene samples subjected to relatively low doses (up to 1320 Mrad), consist chiefly in a lowering

of the Young's modulus. This is related essentially to a reduction of the degree of crystallinity as a result of irradiation (as the density data and the increase of height of the damping peak indicate) and with the plasticizing action exerted by the low molecular weight degradation products, formed in the course of irradiation.

The slight shift of the glass transition point T_g towards lower temperatures observed in the samples irradiated with relatively low doses, is to be ascribed to the same radiation actions, although, as the doses employed are all higher than the critical dose corresponding for gelation of the material,² a certain number of crosslinks per chain is present in the samples considered, whose effects are opposite to those due to the destruction of crystallinity with respect to this plasticizing effect.

In the samples receiving higher radiation doses, however, the effect of the network formation prevails over the decrease in crystallinity, and the Young's modulus increases with increasing dose.

The fact that in the initial stages of irradiation, the effect of crystallinity reduction on the elastic modulus should largely overcome that due to crosslinking is quite reasonable. In fact, in the samples of polypropylene submitted to the lowest radiation doses the crystallinity is still quite high and the crystallites, being interconnected, form a continuous phase, which has a large effect on the modulus. In the samples submitted to higher doses, however, the residual crystallites, fragmented by the irradiation, constitute a dispersed phase, which behaves, from the point of view of their effect on the modulus, as an inert filler of relatively high elastic modulus.

In conclusion, for a given reduction of the degree of crystallinity, the lowering of the modulus should be higher, the higher the initial crystalline/amorphous ratio is.

This is confirmed by comparison of the density and of the modulus data (Fig. 1). In these samples, while the density remains almost constant, the Young's modulus decreases to a large extent.

It should be noted that in all the examined samples, receiving the highest radiation doses, the mechanical spectrum is typical of that for semicrystalline polymers. In particular, at temperatures above the glass transition point, after complete relaxation of the modulus (T_s), the latter, contrary to the elasticity theory, which predicts an increase of the elastic modulus in crosslinked amorphous rubbers with increasing temperature, still decreases with increasing T . The negative temperature coefficient of the modulus can be reasonably explained by the presence of a certain number of crystallites and particularly with the decrease of the crystalline/amorphous ratio with increasing temperature.

On the basis of the present results, it can be considered that in isotactic polypropylene receiving radiation doses up to about 2000 Mrad, at room temperature, the crystallinity be not completely destroyed.

In conclusion, as concerns the shape of the mechanical spectrum of polypropylene, no important changes are produced by the irradiation, except for the samples submitted to high radiation doses, which exhibit a

low temperature loss region; this however does not seem to be of great significance. The latter may be due to the formation of a certain number of short branchings and/or to the diffusion of low molecular weight products produced by radiolysis.

Polystyrene

In isotactic polystyrene, very slight modifications of the dynamic mechanical properties at room temperature are observed. This is due to the fact that polystyrene, at this temperature, is much below its glass transition point, so the structural changes provoked by the irradiation (crosslinking and eventual reduction of crystallinity), cannot largely modify the values of the elastic and anelastic parameters.

The small lowering of E values at all temperatures and the shift of the α peak towards higher temperatures with increasing radiation dose (observed in samples subjected to high radiation dose) indicate respectively a partial destruction of crystallinity and formation of crosslinks in these samples. From x-ray examination a gradual decrease of degree of crystallinity with increasing dose (from about 40% in the unirradiated samples to about 20% in the samples irradiated with 300 Mrad) has been found. This lowering of crystallinity, however, is not evident from density data.

As regards the low-temperature δ relaxation effect, the increase in height of the relative loss peak with increasing radiation dose may be associated with the reduction of crystallinity as a result of the irradiation, if such a phenomenon can be considered to be mainly due to motions in amorphous regions. This seems to be case; in fact, the δ damping peak of the unirradiated quenched sample, which is amorphous, exhibits the maximum height.

The fact that the δ damping peak temperature remains practically unchanged with increasing radiation dose indicates a constancy of the activation energy of the molecular process associated with this phenomenon in all samples. Evidently, the relaxation mechanism responsible for the δ process is not much influenced by factors affecting interchain barriers or intermolecular cohesion; it is, however, strongly influenced by intrachain barriers, as it has been recently demonstrated by investigations made in our laboratory on some ring-substituted polystyrenes and other polymers containing benzene rings in the side chains.¹⁷⁻¹⁹

Polybutadiene

The lowering of E values at room temperature in *trans*-1,4-polybutadiene, during the early stages of irradiation, is due mainly to the reduction of the crystalline/amorphous ratio (as density data indicate), whose effect is greater than the opposite effect due to the crosslinking. On the contrary, the successive increase of Young's modulus with increasing radiation dose (for R above 400 Mrad) can be attributed to the greater effect of the network formation.

It should be noted that at room temperature, irradiated polybutadiene behaves as a crosslinked, partially crystalline rubber; the elastic modulus,

then, depends on both degree of crosslinking and crystallinity. It may be related to these quantities by a relation of the type²⁰:

$$E = d(RT/\bar{M}_c)(1 + AX + BX^2)$$

where d is the density, R the gas law constant, \bar{M}_c the number-average molecular weight between crosslinks, X the volume fractions of crystallites, and A and B are constants.

For evaluating the two effects separately, a comparison of the elastic modulus of the various specimens should be made at temperatures above the melting point of residual crystallites and at temperatures sufficiently lower than the glass transition point. In the former case, the effect of crystallinity on elastic modulus is nil; in the latter case, at contrary, it is the effect of the crosslinks which can be neglected.

From the high temperature values of the elastic modulus of the irradiated specimens (Fig. 13), it can be observed that, except for the first two samples (1 and 2), whose crosslink density is not sufficient to hinder chain slipping, in all the other specimens the Young's modulus increases with increasing radiation dose adsorbed. At low temperature (-100°C .), on the other hand, the Young's modulus, in the early stages of irradiation (up to 600 Mrad of irradiation dose adsorbed), decreases with increasing R , because of the lowering of the crystalline/amorphous ratio. For doses higher than that limit, it remains practically constant (Fig. 12), as these samples are practically amorphous, and the difference in degree of crosslinking has no effect on the value of the elastic modulus.

Of some interest is the comparison of the mechanical spectra of the samples irradiated with doses up to 600 Mrad and that relative to the un-irradiated polybutadiene sample (Fig. 10).

The X loss peak, due to the crystalline phase transition, tends to disappear because of the progressive reduction of the crystallinity by the irradiation, as is also indicated by the E - T curves. The α' peak seen in the irradiated samples can be reasonably attributed to the melting of residual crystallites.

The increase of the height of the α damping peak and its shift towards higher temperatures may be related respectively with the reduction of the crystallinity and with the increase of the mean apparent activation energy associated with this transition, because of the sterical hindrance of crosslinks.

The secondary relaxation effect γ observed at about -100°C . in the irradiated samples may be attributed to the formation, by irradiation, of $-\text{CH}_2-$ sequences in the main chain, the motion of which gives rise to a mechanical relaxation effect at that temperature (at the frequency employed by us).²¹ This is confirmed by the fact that the initial insaturation decreases with increasing radiation dose and also by the fact that a mechanical spectrum very similar to that of the irradiated polybutadienes is shown by samples of this same material subjected to partial hydrogenation

(Fig. 14). On the basis of these results the irradiated polybutadienes may be regarded as crosslinked ethylene-butadiene copolymers.

One particular aspect of the radiochemical crosslinking in comparison with the conventional vulcanization with sulfur consists in the fact that, while in the vulcanized products the glass transition point T_g is shifted towards higher temperatures with increasing content of combined sulfur, in the irradiated samples this point remains practically unchanged on the temperature scale, as the crosslink density increases. Evidently, in the vulcanization with sulfur, in addition to the formation of crosslinks between chains, there is also a marked increase of intermolecular cohesion due to the formation of strong polar groups along the chain. This is confirmed by the dielectric data for vulcanized rubbers, which indicate an increase of the

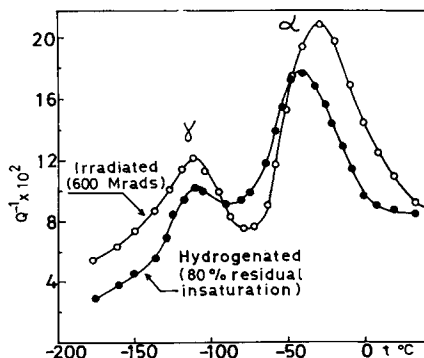


Fig. 14. Damping factor in irradiated and in hydrogenated *trans*-1,4-polybutadiene as function of temperature.

dielectric constant and dielectric loss with increasing degree of vulcanization because of the increase of the orientational polarizability of the molecules.

A similar effect has been found by Schmieder and Wolf in the examination of the dynamic mechanical properties of irradiated natural rubber.²²

In the specimen receiving the highest radiation doses (Fig. 11), the decrease of height of the loss peaks may be associated with the reduction of the number of the chain elements capable of contributing to the corresponding relaxation, because of the excessive crosslinking. The widening of the relaxation region however, is associated with the widening of the relaxation time band.

CONCLUSIONS

From the discussion of the experimental data it can be seen that irradiation produces no significant modification of properties in isotactic polypropylene and isotactic polystyrene.

To the contrary, of great interest are the structural modifications produced in *trans*-1,4-polybutadiene. First of all, the existence in the irradiated polymers of a remarkably low-temperature relaxation in effect, whose importance becomes comparable with the main relaxation effect, is expected to be accompanied by a noticeable improvement of the mechanical properties of polybutadiene at low temperature, specially as concerns brittleness. It has, in fact, been demonstrated that, in polymer showing important low-temperature relaxation effects connected with motions in the main chain, the brittle point is, in general, shifted towards temperatures much lower than the glass transition point.²³ This suggestion is confirmed by the fact that hydrogenated polybutadienes (whose mechanical spectrum we proved to be very similar to that of the corresponding irradiated material) show a much improved low-temperature performance as concerns mechanical properties as compared with polybutadiene itself.²⁴

Moreover, the fact that the intermolecular cohesion is not increased by effect of radiochemical crosslinking, in contrast to what happens with the conventional sulfur vulcanization, may have a noticeable influence on the elastic properties of polybutadiene rubbers.

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Résumé

Le module de Young et le facteur de l'amortissement mécanique ont été déterminés entre -180 et $+280^{\circ}\text{C}$ (à des fréquences de quelques kHz) pour des échantillons de polypropylène isotactique, polystyrène isotactique et *trans* 1,4-polybutadiène, soumis à des radiations γ par irradiation par pile et par des neutrons avec des doses γ de 90 à 4000 Mrads. Dans le cas du polypropylène isotactique, on n'a pas pu obtenir de variations de structure importante par suite d'irradiations sur une destruction partielle de la cristallinité. Les échantillons soumis à des doses d'irradiation élevées montrent une région de perte à basse température qui est attribuée à la formation d'un certain nombre de ramifications par suite de l'irradiation. Le polystyrène isotactique montre de très faibles modifications et des propriétés dynamiques mécaniques à température de chambre. À basse température, une augmentation de l'intensité du phénomène de relaxation (probablement dû à l'oscillation des anneaux aromatiques) a été observée avec un accroissement de dose d'irradiation. Des importantes modifications structurales provoquées par la radiation, la destruction de la cristallinité accompagnée de pontage qui transforme le matériau en un caoutchouc ponté ont été observés dans le cas du polybutadiène 1,4-*trans*. Contrairement à la vulcanisation conventionnelle sous l'influence du soufre, le pontage par radiation ne cause pas un glissement notable du point de transition vitreuse. Un second effet de relaxation à basse température, qui n'existe pas pour un matériau non irradié apparaît dans les courbes de perte mécanique des échantillons irradiés; il est attribué à la formation de séquences $-\text{CH}_2-$ dans la chaîne principale par suite de la saturation des liaisons $\text{C}=\text{C}$. Le spectre mécanique du polybutadiène irradié est très semblable à ceux montrés par les copolymères éthylène-butadiène pontés.

Zusammenfassung

Der Young-Modul und der mechanische Dämpfungsfaktor wurde zwischen -180 und 280°C (bei einer Frequenz von einigen kHz) an Proben von isotaktischem Polypropylen, isotaktischem Polystyrol und *trans*-1,4-Polybutadien bestimmt, welche einer Reaktorbestrahlung (γ -Strahlen und Neutronen) mit γ -Dosen von 90 bis 4000 Mrad unterworfen worden waren. Bei isotaktischem Polypropylen wurden durch die Bestrahlung mit Ausnahme einer partiellen Zerstörung der Kristallinität keine wesentlichen Strukturänderungen erzeugt. Proben, die der Einwirkung hoher Strahlungsdosen unterworfen worden waren, zeigen einen Tieftemperaturverlustbereich, welcher auf die Bildung einer gewissen Zahl von Verzweigungen durch die Bestrahlung zurückgeführt wird. Isotaktisches Polystyrol zeigt eine sehr schwache Modifizierung der dynamisch-mechanischen Eigenschaften bei Raumtemperatur. Bei niedriger Temperatur wird eine Zunahme der Intensität des " δ "-Relaxationsphänomens (wahrscheinlich wegen der Oszillation der Phenylringe) mit steigender Bestrahlungsdosis beobachtet. Weitgehend durch die Bestrahlung hervorgerufene Strukturmodifikationen, von einer Vernetzung begleitete Zerstörung der Kristallinität, welche das Material in einen vernetzten Kautschuk umwandeln, werden bei *trans*-1,4-Polybutadien beobachtet. Im Gegensatz zur konventionellen (Schwefel-) Vulkanisation verursacht die Vernetzung durch Strahlung keine merkliche Verschiebung des Glasumwandlungspunkts. Ein sekundärer Tief-

temperatureffekt, der beim nichtbestrahlten Material nicht vorhanden ist, tritt in den mechanischen Verlustkurven der bestrahlten Proben auf; er wird auf die Bildung von $-\text{CH}_2-$ Sequenzen in der Hauptkette durch Sättigung von $\text{C}=\text{C}$ -Bindungen zurückgeführt. Das mechanische Spektrum von bestrahltem Polybutadien ist demjenigen von vernetzten Äthylen-Butadiencopolymeren sehr ähnlich.

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