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The Production of Graft Copolymers from Poly-α-olefin Hydroperoxides

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Linear polymers and copolymers of the α-olefins present the interesting characteristic that one-half of the carbon atoms belonging to the main chain are tertiary carbon atoms to which an electron-releasing alkyl group is linked. Tertiary carbon atoms of the same type are contained, although to a lesser extent, in the copolymers of the α-olefins with ethylene. The hydrogen atom linked to such tertiary carbon atoms shows a greater reactivity, compared to the hydrogen of a CH_3 or CH_2 group. Such reactivity of the hydrogen can be considered as an inconvenience with regard to the aging stability at high temperature of the unstabilized polymers; however, it can be utilized to modify the properties of poly-α-olefins particularly the surface properties and to prepare a very large series of grafted or reticulated derivatives. In 1954, shortly after the first preparations of isotactic polypropylene and polybutene, we had already started to study the thermal and catalytic peroxidation of such polymers, taking advantage of the experience previously acquired in studying the low temperature peroxidation of cumene.[1]

It has been proved that the autohydroperoxidation of the poly-α-olefins can be interpreted according to the kinetic schemes described by Bolland and Gee[2] and that this shows, in certain aspects, some analogies with the peroxidation of other saturated hydrocarbons containing tertiary carbon atoms, such as 1,4-dimethyl-cyclohexane, studied by Stannett, Woodward, and Mesrobian.[3] Such analogies hold more accurately for polymer solutions, and in such cases, we have observed a zero-order reaction with respect to the oxygen pressure. By peroxidation of non-dissolved polymers, in particular highly crystalline polymers in the solid state, it has been possible to observe an influence of the oxygen pressure, probably due to the influence of the pressure on the diffusion rate of oxygen inside the samples.

The bimolecular mechanism of hydroperoxide decomposition which, in the case of dimethylcyclohexane, prevails at low temperatures, would seem to be less probable in the case of crystalline poly-α-olefins for which the association of the hydroperoxidic groups is hindered by the low mobility of those molecules which are part of crystals. This can be one of the reasons of the limited degradation and of the consequent slight change with aging of the mechanical properties of the crystalline polymers of high molecular weight slightly peroxidized at low temperature.

Monomolecular dissociation of the hydroperoxide does not take place or occurs reversibly at low temperature in the absence of free radical-capturing substances. However, grafting takes place rapidly in the presence of monomers which can be polymerized by free radicals, even at relatively low temperature.

In the study of hydroperoxidation with air or oxygen, we have observed that peroxidation can be carried out, without substantial degradation by operating at a temperature lower than 70–80°C. In such conditions, the peroxidation of the crystalline isotactic polymers takes place only on the surface of the crystals or in the intercrystalline amorphous regions next to the external surface. On the contrary, in the crude polymers containing stereoblock and atactic polymers, the peroxidation takes place deeper, depending on the stereoisomeric composition. This is related to the solubility and the diffusion rate of oxygen.

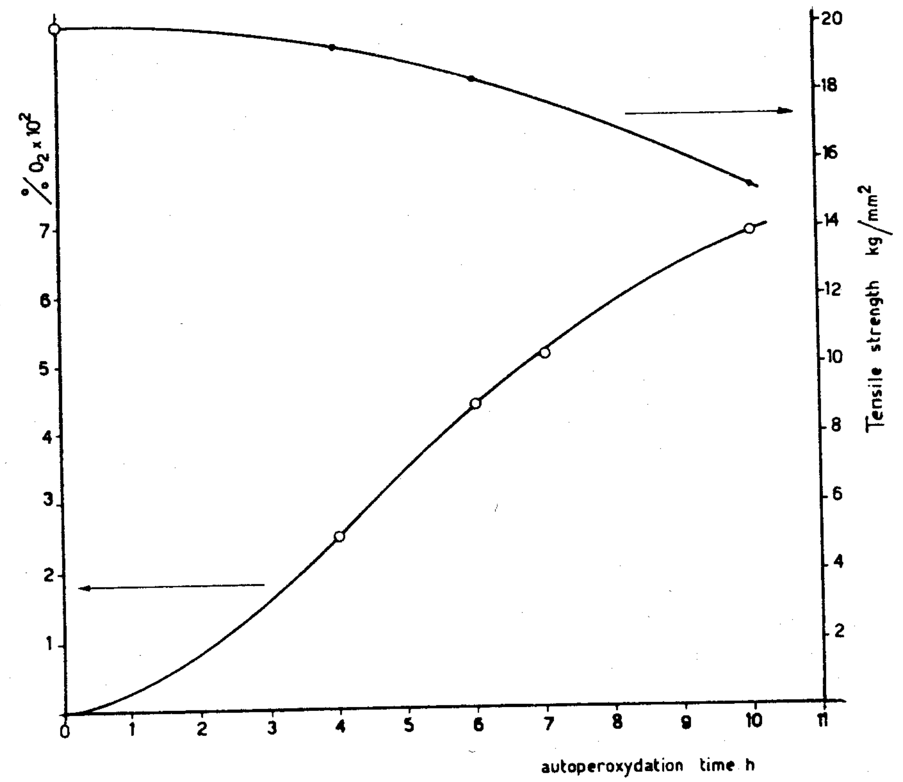

Fig. 1. Surface autoperoxidation at 70°C. and 3 at. air pressure on oriented 0.016 cm.-thick sheets of crystalline polypropylene (85% insoluble in boiling *n*-heptane).

In Figure 1 are reported the results of mainly superficial hydroperoxidation on laminae of crystalline polypropylene (85% insoluble (in boiling heptane) oriented by stretching and having a maximum tensile strength of 20 kg. mm.^{2} and an elongation of 27% in the direction of stretching. The peroxidation was carried out at temperature of 70°C. and an air pressure of 3 atmospheres. The mechanical characteristics remained practically unchanged (the decrease was not more than 10%) for oxygen contents up to

0.035 weight-% of oxygen present as peroxide or hydroperoxide groups. A decrease of more than 20% in the tensile strength of the initial product takes place in the oxygen content, as defined above, exceeds 0.05%.

The peroxidation in such products does not take place homogeneously and, most probably, mainly concerns the surficial regions to a depth of the order of 0.001 mm. This is also proved by the fact that, in the hydroperoxidation of a filament having a diameter of 0.025 mm. it is possible to reach oxygen contents about 10 times higher, without remarkable change of the mechanical characteristics. This behavior can be explained by considering the difference in the surface area/weight ratio existing in the tested filaments and laminae. In fact, the oxygen content referred to the external surface reaches about the same values in both cases. In the course of tests carried out at a temperature of 75–85°C. on a polypropylene filament having a resistance of 5.9 g./den., one observes that at oxygen contents up to 0.4 weight-%, the resistance remains almost unchanged (the decrease is not higher than 10%). The influence of pressure on the peroxidation rate is less important on samples having a high surface-volume ratio, such as filaments.

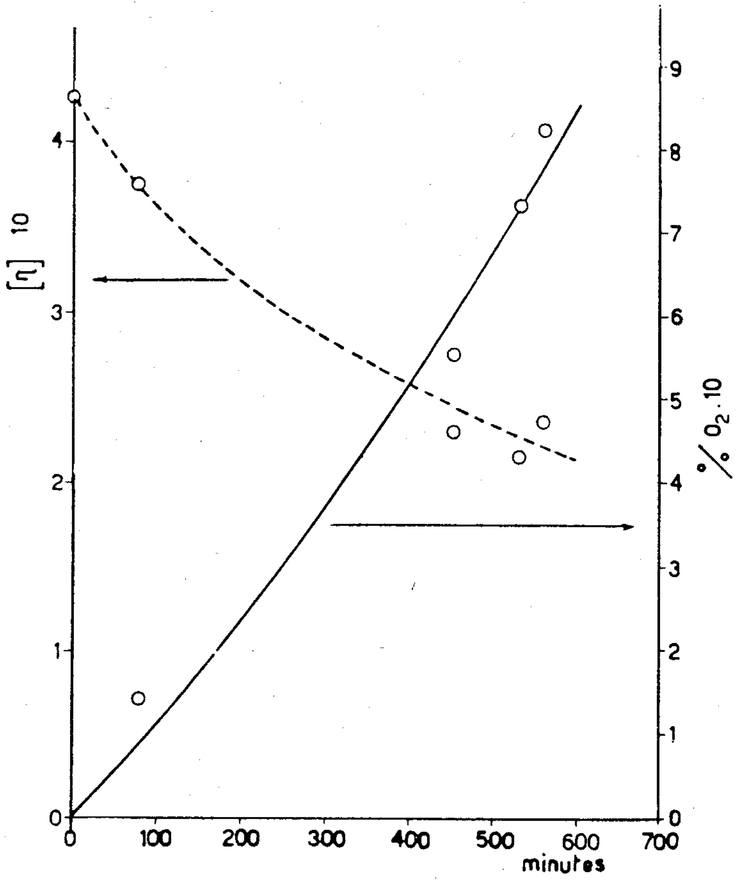

Fig. 2. Hydroperoxidation of atactic polypropylene dissolved in isopropylbenzene (concentration 15.5%) containing 4% methanol at 70°C. in stainless steel vessel under air pressure.

Although the filaments under examination contained almost 85% of crystallizable isotactic polymer (insoluble in boiling heptane), hydroperoxidation took place chiefly on the amorphous part. In fact, almost one-half of the fixed oxygen is linked to the atactic polymers (extractable by ether) present in the sample in very small amounts (about 5–6%).

Peroxidation can be achieved in a more homogenous way, if it is carried out in solution, in the presence of initiators. A suitable method for rapid peroxidation of α-olefin polymers on a laboratory scale consists in operating in cumene solution (and also in the presence of small quantities of preformed cumene hydroperoxide). The presence of a small percentage of methanol (3–5% with respect to cumene) inhibits side reactions.[1] Under such conditions, by bubbling air at atmospheric pressure into a 15–20% solution of the polymer, peroxidation occurs rapidly at a temperature of 65–70°C. (Fig. 2). It is interesting to point out that cumene hydroperoxide and the poly-α-olefin hydroperoxides act mutually as catalysts, since the cumene hydroperoxide catalyzes the α-olefin peroxidation, while the hydroperoxidized poly-α-olefins catalyze the cumene peroxidation.

The suitability of such a laboratory method is evidenced by the fact that, under the same conditions, it is possible to hydroperoxidize polystyrene also. In tests carried out on 30% solutions of an atactic polystyrene with a low average viscometric molecular weight (10,000) in cumene, hydroperoxide contents of 2–4 weight-% (corresponding to 6–12

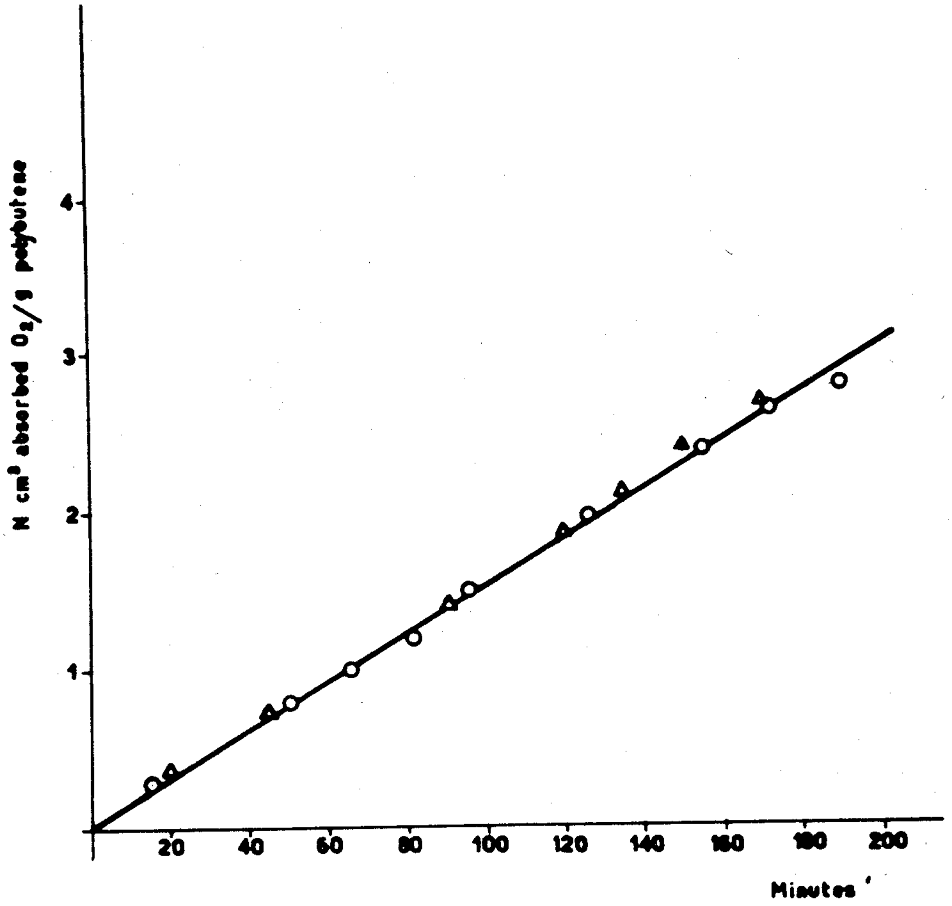

Fig. 3 Hydroperoxidation of poly-α-butene (residue after extraction with ethyl ether) $[\eta]_{75°C.}^{toluene} = 4.5$; X-ray crystallinity = 45%; initiator: Bz_2O_2: (O) temperature 83°C. after induction period of 10 min.; (Δ) temperature 83°C. after induction period of 20 min.

TABLE I

Air Pressure Hydroperoxidation of 34% Polystyrene Solutions in Isopropylbenzene Containing 4% Methanol at 70°C. in Stainless Steel Vessels

Temperature, °C.	Time, minutes	Hydroperoxide groups, weight-%	[η], initial[a]	[η], final[a]
70	240	1.98	0.095	0.095
70	460	4.03	0.095	0.0875
80	600	1.03	1.07	0.575

[a] Viscosities have been determined in benzene at 34°C.

hydroperoxide groups/100 styrene monomeric units) can be obtained easily without significant degradation (Table I). In the literature, less highly peroxidized derivatives of polystyrene, containing 1.6 peroxidic groups/100 styrene units, have been previously described.[4]

The sharing of oxygen between polymer and cumene takes place at different rates for the different polymers. Under the above-mentioned conditions, the oxidizability of polystyrene, referred to the monomeric unit, seems to be higher than that of polypropylene.

In case of such polymers as partially crystalline polybutene, which are easily swollen or soaked by initiator solutions, a rather homogeneous hydroperoxidation can be achieved with air. Figure 3 shows the oxidation data of two samples of polybutene, (the residue after ether extraction having 45% x-ray crystallinity), in presence of benzoyl peroxide at 83°C. and 3 atmospheres oxygen. The hydroperoxidized samples, after elimination of undecomposed benzoyl peroxide, show an O_2 content of 0.4%, which is very close to the quantity of oxygen absorbed.

The hydroperoxidized polymers can be used as initiators for peroxidation reactions and can supply a variety of products by grafting. It is convenient, in order to describe the different types of products, to consider the peroxidized α-olefin polymers separately according to their stereoisomeric structures: (*a*) crystalline isotactic polymers and (*b*) atactic polymers and stereoblock polymers.

GRAFTING ON ISOTACTIC α-OLEFIN POLYMERS

The surface hydroperoxidation of manufactured articles from isotactic polymers makes it possible to modify the surface properties by grafting to produce, *e.g.*, hydrophilic fiber or films, dyeable fibers, etc. A concentration of 0.01–0.02 g. oxygen/m.^{2} of surface is, generally, sufficient to obtain a thickness of grafted polymers on the surface which, according to the conditions and to the type of monomer used, can vary from 0.01 to 0.1 mm.

Some data of grafting on laminae, achieved by immersing the surface of the polymer in solutions of the monomer to be grafted, are reported in Table II and Figure 4. The grafted products were washed with solvents to

TABLE II

Grafting of Methyl Methacrylate at 70°C. on Surface-Peroxidized Polypropylene Sheets

Peroxidized poly-α-olefin						Mechanical properties of the grafted product		
Hydroperoxide groups, weight-%	Ultimate tensile strength, kg./mm.^{2}	Elongation at break, %	Grafting time, hr.	Initial thickness, mm.	Final thickness, mm.	Weight increase, %	Ultimate tensile strength, kg./mm.^{2}	Elongation at break, %
—	20.0	27	—	0.16	—	—	—	—
0.0235	19.3	46.5	2	0.16	0.20	44.6	14.1	44.5
0.0268	17.1	41.2	2	0.16	0.23	48	12.45	58.9
0.0542	15.3	41	2	0.17	0.23	50	11	47
0.0156	20.8	29.5	3	0.16	0.45	149	7.4	50
0.0204	18.4	35.2	3	0.16	0.40	150	8.8	59
0.0345	18.4	27.0	3	0.15	0.42	162	6.13	68.8

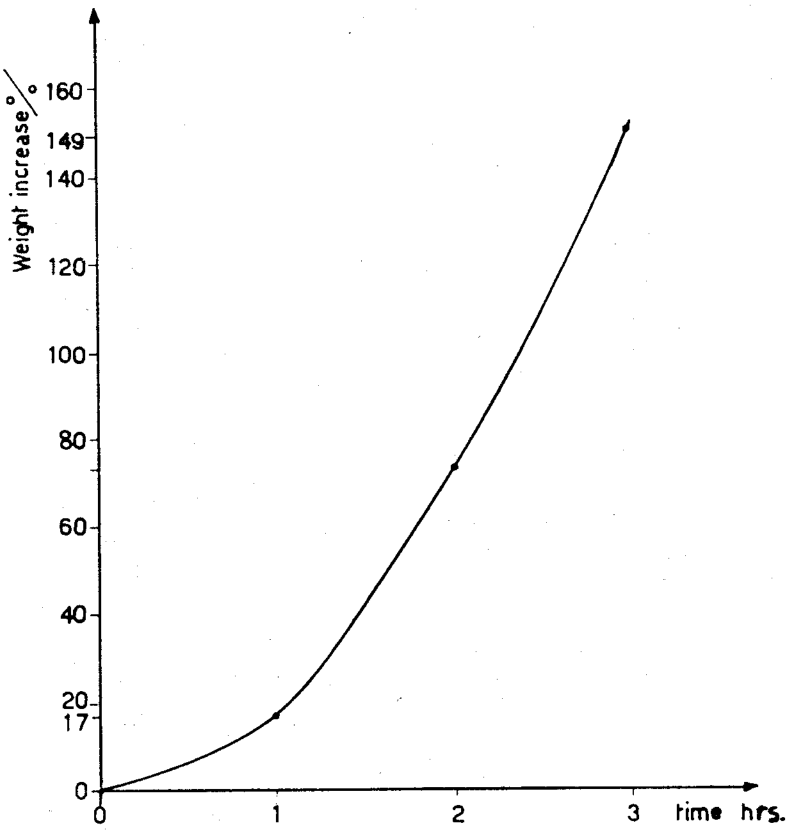

Fig. 4. Weight increase of hydroperoxidized polypropylene sheets, thickness 0.16 mm. (hydroperoxide content 0.038 g./m.^{2}) by methyl methacrylate grafting at 70°C.

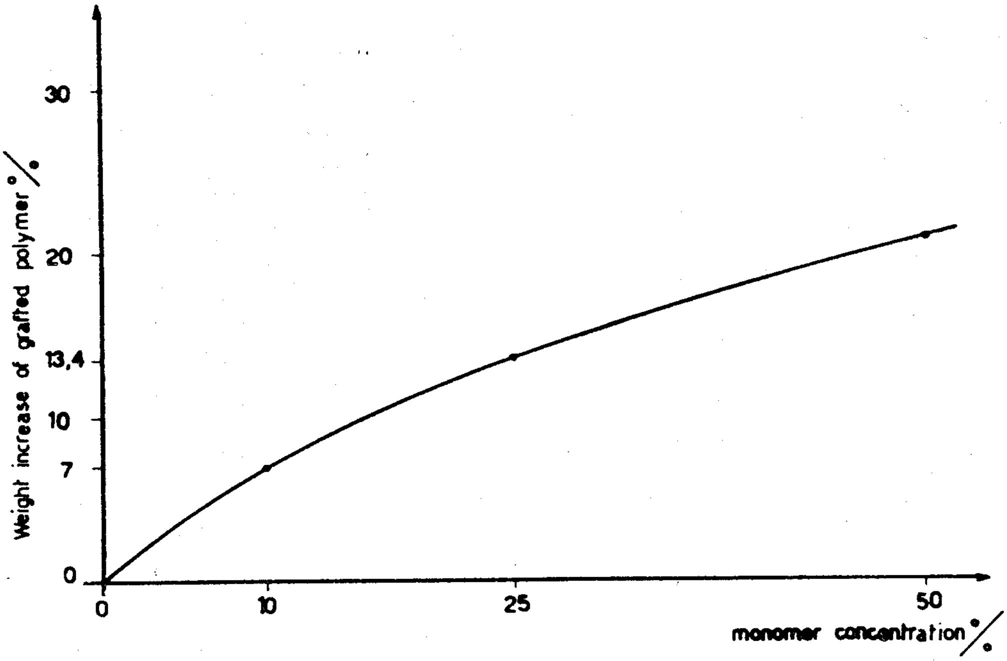

Fig. 5. Grafting of methyl methacrylate in toluene on polypropylene autoperoxydized fiber. Hydroperoxide content: 0.0159 g./m.^{2}; grafting temperature: 75°C.; time: 20 hr.

remove the monomer and, in some cases, the homopolymer of the monomer used for the grafting.

Moderate grafting, unless followed by thermal treatment, does not greatly modify the ultimate tensile strength and elongation of a filament. The increase in section due to the grafting does not contribute appreciably, therefore, to the mechanical resistance of the filament.

The increase of the hydroperoxide content from 0.01–0.02 g./m^2. to values of 0.3–0.5 g./m.^{2} causes only a slight increase of the grafting rate. A variation of the weight of grafted polymer can be obtained by varying the monomer concentration or the time (Fig. 5).

GRAFTING ON ATACTIC α-OLEFIN POLYMERS

The high linearity of α-olefin atactic polymers and copolymers obtained by the coordinated anionic catalysis processes and the ease with which they can be hydroperoxized, both in solution as well as in the dry or slightly swollen state, make them suitable for the production of very interesting grafted polymers. The simplest method of preparing these polymers is to dissolve the hydroperoxide of poly-α-olefin containing 0.2–0.4% of peroxidic oxygen in the monomer and to operate under the normal polymerization conditions (*e. g.*, emulsion, suspension, or block polymerization).

The hydroperoxide groups present in the poly-α-olefin polymers act as polymerization initiators. Comparative tests of styrene polymerization with or without peroxidized poly-α-olefin present show the following to be true.

(1) In the presence of unperoxidized poly-α-olefin, styrene does not polymerize at a temperature of 80–90°C. if no initiator is present. The addition of conventional initiators causes the formation of principally homopolymers of styrene. In fact, the mechanical properties (*e.g.*, impact strength) of the polymers thus obtained are not improved, as compared with conventional poly-styrenes.

(2) In the presence of peroxidized poly-α-olefins (10–12 weight-%) and under nitrogen at a temperature 80–90° there is formation of grafted polystyrenes possessing high impact strengths.

It is interesting to note that, while the high impact strength polystyrenes obtained by copolymerization with or grafting of styrene on unsaturated rubbers show, in general, a low stability to aging, as shown by the variation of the physical properties with time (*i.e.*, of the sound velocity), the polystyrenes grafted on α-olefins show mechanical properties which do not vary with aging.

In Table III are reported some properties of grafted polystyrenes. The use of α-olefin polymers with intrinsic viscosity >1 appears to be useful for obtaining grafted polystyrenes having high resilience. The use of low crystalline poly-α-olefins lead to a greater increase in resilience and the grafted polystyrenes so obtained show a smaller loss in hardness than the conventional graft polymers.

TABLE III

Grafting of Styrene on Peroxydized Poly-α-Olefins

	Peroxidized poly-α-olefin used for grafting				Grafted polystyrene on poly-α-olefins			
Polymer	Crystallinity (x-ray), %	Hydroperoxide groups, weight-%	[η]	Poly-α-olefin, %	Grafting temperature, °C.	Time, hr.	Rockwell hardness	Impact strength,[f] kg.-cm./cm.^{2}
—	—	—	—	—	—	—	70–80 M	10[g]
Polypropylene[c]	0	0.288	0.36[d]	12	80	44	n.d.	30
C_2–C_3 copolymer	10	0.206	1.04[d]	12	80	50	n.d.	30
Polybutene[c]	0	0.402	0.36[d]	12	80	48	42 M	34
" [a]	25	0.515	0.64[d]	12	90	50	51 M	40
" [a]	25	0.412	0.65[d]	12	90	50	48 M	55
" [a]	25	0.412	0.77[d]	12	90	50	41 M	40
" [a]	25	0.382	0.82[d]	8	80	52	49 M	29
" [a]	25	0.382	0.82[d]	11.5	80	52	22 M	>100
" [a]	25	0.247	1.18[d]	12	80	48	17 M	>100
" [b]	44	0.247	1.38[e]	12	90	50	77 L	40

[a] Residue after extraction with acetone (mixture of atactic and isotactic polymers).

[b] Residue after extraction with ethyl ether (isotactic and stereoblock).

[c] Atactic polymer.

[d] Viscosities determined in tetralin at 135°C.

[e] Viscosities determined in toluene at 75°C.

[f] Impact strength measured on 3 × 12.75 × 125 mm. unnotched specimens with a Charpy pendulum.

[g] Ungrafted polystyrene.

TABLE IV

Grafting of Vinyl Chloride on Hydroperoxidized Poly-α-Olefins

Peroxidized poly-α-olefin used for grafting					Reaction conditions			Grafted polymer residue after extraction with ethyl ether				
Polymer	Hydroperoxide groups, weight-%	$[\eta]^a$	Weight of polymer, g.	Vinyl chloride, g.	Polyamine, g.	Grafting temperature, °C.	Time, hr.	Chlorine in polymer, %	PVC content in polymer, %	Polymerized monomer, %	Grafted poly-α-olefin, %	$K_{Fikentscher}{}^b$
Polypropylene	0.41	0.24	15	180	0.4 TEP^c	46	30	54	95	66	42	84.5
Polybutene	0.206	0.71	12	180	0.24 TEP^c	37–46	24	52	91.5	60	83.5	84
Polybutene	0.206	0.57	12	135	0.25 TEP^c	53	24	47.6	83.5	29.3	65	79
Polybutene	0.206	0.60	7.5	180	0.15 TET^d	46	24	54.2	95	79	100	79
Polybutene	0.206	0.60	7.5	180	0	75	24	54.5	96	13.4	13.4	56

[a] Measured in toluene at 75°C.

[b] Viscosity of polyvinyl chlorides measured in cyclohexanone at 30°C.

[c] TEP = Tetraethylene pentamine (Delta chemical).

[d] TET = Triethylene tetramine (Eastman Organic Chemicals).

It is particularly interesting to examine the products obtained by grafting of vinyl chloride on poly-α-olefin, because of the difference in solubility as compared to the homopolymers. Such grafting proves to be rather difficult, and it is necessary to adopt particular conditions to avoid the formation of vinyl chloride homopolymers to the exclusion of grafting. The high solubility of amorphous poly-α-olefins in aliphatic hydrocarbons allows the non-grafted poly-α-olefins to be separated with ease from the homopolymers and from the grafted polymer of vinyl chloride. A separation, at least in part, of the last can be carried out, although less easily, by dissolution or by fractional precipitation of solutions in ketonic solvents. If the polymerization is carried out in an aqueous emulsion in the presence of polyethylenamines, grafting occurs in preference to homopolymer formation (Table IV).

The plasticizing action of the poly-α-olefins bound to the grafted polyvinyl chloride (PVC) is quite different from that of the conventional PVC plasticizers. The latter contain polar groups which tend to form association complexes with the polar groups of the polyvinyl chloride, thus behaving as good solvents. On the contrary, the poly-α-olefins do not show any affinity with polyvinyl chloride and would separate out if they were not grafted. The grafting prevents the separation of the poly-α-olefins; these in turn, do not prevent the association of the polyvinyl chloride chains among themselves. As a consequence, the lowering of the second-order transition temperature is not observed as it is with the conventional plasticizers, an increase in resilience and ultimate elongation, and a relatively small reduction of the ultimate tensile strength are noted.

The variety of problems in which this institute has been interested in recent years, has compelled us to limit this study to only a first orientative survey concerning the problems of grafting. Nevertheless, it seems that the methods we have employed look more interesting than those which utilize high energy radiations or initiators with a low molecular weight. Also, the results of studies of reticulation of α-olefin polymers by chemical methods appear more interesting than those involving high energy radiation. The high number of tertiary carbon atoms very clearly differentiates the poly-α-olefins from polyethylene, especially when highly crystalline, and makes the poly-α-olefin more sensitive to chemical reticulation and grafting processes which are milder and more easily controlled than high energy radiation processes.

References

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(3) V. Stannett, A. E. Woodward, and R. Mesrobian, *J. Phys. Chem.*, **61,** 360 (1957).

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Synopsis

The catalytic and autocatalytic hydroperoxidations of the surface of filaments and laminae of isotactic and stereoblock poly-α-olefins have been studied. The peroxidation of atactic and stereoblock polymers in solution has also been examined. Peroxidized polymers have been used as radical initiators in the polymerization of vinyl monomers to achieve their grafting on poly-α-olefin chains. Some properties of these graft polymers, e.g., antishock properties of polystyrenes grafted on poly-α-butene, have been reported.

Résumé

On a étudié les hydroperoxydations catalytiques et autocatalytiques de la surface de filaments et de lames de poly-α-oléfines isotactiques et à stéréobloc. On a également examiné la peroxydation de polymères atactiques et à stéréobloc, en solution On a employé des polymères peroxydés, comme initiateurs radicalaires, dans la polymérisation de monomères vinyliques, pour réaliser leur greffage sur des chaînes poly-α-oléfiniques. On a signalé quelques propriétés de ces polymères greffés, telles par exemple, les propriétés antichocs de polystyrènes greffés sur du poly-α-butène.

Zusammenfassung

Die katalytische und autokatalytische Bildung von Hydroperoxyden an der Oberfläche von Fäden und Filmen aus isotaktischen und Stereoblock-poly-α-olefinen wurde untersucht. Ebenso wurde die Peroxydbildung an ataktischen und Stereoblockpolymeren in Lösung untersucht. Polymere mit Peroxydgruppen wurden als Radikalstarter bei der Polymerisation von Vinylmonomeren verwendet, um deren Pfropfung auf die Poly-α-olefinketten zu erreichen. Einige Eigenschaften dieser Graftpolymeren, z.B. Schlagfestigkeitseigenschaften von Polystproben, die auf Poly-α-Buten aufgepfropft wurden, werden mitgeteilt.

Discussion

G. Natta (*Milan*): Some measurements which we have made on the catalytic peroxidation of polybutene-1 proved that the peroxidation of the solid polymer with air at atmospheric pressure yields almost exclusively hydroperoxidic groups initially, while, as the oxygen content increases, the peroxidic groups increase progressively. These results were obtained (*a*) by titration of the hydroperoxidic groups with triethyl arsines which are specific reagents for the hydrperoxidic groups [Horner and Jurgens, *Angew. Chemie,* **70,** 266 (1958)], and (*b*) by determination of the total peroxidic oxygen (hydroperoxides plus peroxides) by titration with hydriodic acid. Infrared examination has qualitatively confirmed the results obtained by chemical analysis. In fact, the infrared absorption bands at 2.80 and 3.10 microns (due to O—H and R—O—O—H bands) and the broad absorption in the region between 9.50 and 11.50 microns (due to the presence of peroxidic groups) are all easily detectable. The intensity of this last absorption increases as the content of peroxidic groups, as determined by chemical analysis, increases.

The determination of the molecular weight of peroxidized polymers presents some difficulty in the case of crystalline polymers, owing to their insolubility at low temperature. If, in order to keep crystalline polymers in solution, high temperatures (*e.g.,* 135°C.) are employed, a depolymerization is observed during the determination of the intrinsic viscosity.

In the case of peroxidized amorphous or stereoblock polybutenes-1, we preferred to operate at a lower temperature. The comparison between the values determined at 135°C. and those determined at 75°C. shows a decrease of the intrinsic viscosity of about 50%, due to the depolymerization at the higher temperature.

Table I shows the intrinsic viscosity of the same polymer determined at 75 and 135°C., respectively. The depolymerization of peroxidized polymers, which occurs at high temperature, also takes place during the peroxidation of the sample. Therefore, it is convenient either to carry out the hydroperoxidation or to use peroxidized polymers for the grafting of other polymers at temperatures below 80°C.

TABLE I

Polybutylene Depolymerization during Molecular Weight Viscometric Determination

% O_2, —O—O—	I^a [η]	II^b [η]
<0.02	2.75	2.22
0.26	1.24	0.509
0.78	0.47	0.225
1.13	0.263	0.168

[a] Determination at 75°C. in toluene.

[b] Determination at 135°C. in tetralin.

P. Lebel (*Paris*): La conférence du professeur Natta présente un très grand intérêt d'autant plus grand pour nous que nous étudions la peroxydation des polymères paraffiniques ou aromatiques depuis 1953 (Landler et Lebel, Brevet Français N° 1.101.682, Anglais 791.453, Italien 530.825) et plus particulièrement les différentes oléfines et le polystyrène.

Dès le début, nous avons comme tous les auteurs rencontré de grandes difficultés dans la peroxydation par l'oxygène simplement catalysée par des produits radicogènes ou par la chaleur.

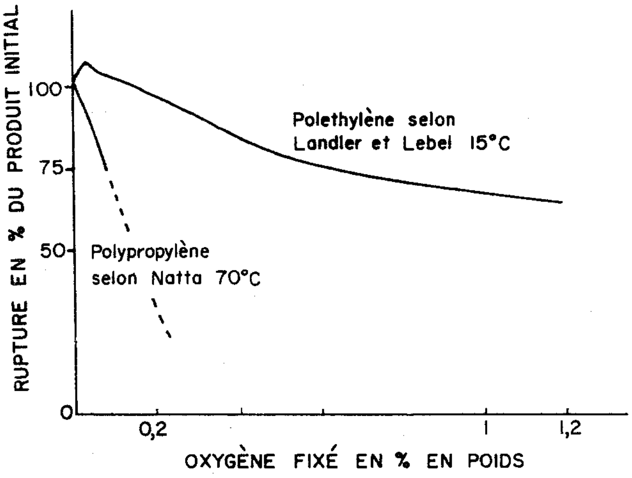

Figure 1.

De plus cette méthode de peroxydation a un inconvénient majeur que le professeur Natta met une fois de plus en évidence, avec ses résultats, la peroxydation par l'oxygène à chaud est toujours accompagnée de ruptures de chaînes, rupture qui est d'autant plus importante que la température est plus élevée ce qui a été parfaitement démontré par les travaux de Hinshelwood et Norrish.

Dans ce cas, autoxydation et dégradation procèdent selon des réactions en chaînes.

Il fallait donc trouver des méthodes de peroxydation qui procèdent différemment et surtout soient utilisables à froid.

Nous en connaissons deux et je citerai la peroxydation par irradiation développée par Chapiro, Magat et Sebban (Brevet Français N° 1.125.537 et 1.130.100) et l'ozonisation que nous avons longuement développée.

Ce sont des résultats obtenus par cette méthode par ozonisation que nous donnons pour comparaison avec les résultats du professeur Natta.

Cas des Polyoléfines. Je me permets de reprendre la courbe 1 du professeur Natta et de la retracer en montrant la variation de résistance à la traction en fonction de la teneur en oxygène.

La courbe du professeur Natta porte sur le polypropylène peroxydé à chaud et la notre sur le polyéthylène ozonisé à froid.

Il est évident que la peroxydation à chaud dégrade beaucoup plus.

Il est seulement regrettable qu'on n'ait dans la peroxydation à chaud que des prises d'oxygène relativement faibles.

On peut noter en outre que l'ozonisation fait perdre au polyéthylène haute pression 50% de sa cristallinité en 12 h d'ozonisation dans des conditions données à 20°C, tandis que la même chute est atteinte en 10′ dans les mêmes conditions d'ozonisation mais à 100°C. En fait $^1/_4$ h à $^1/_2$ h d'ozonisation à froid suffit pour le greffage, la cristallinité est donc entièrement sauvegardée (Landler, résultats à publier).

Polystyrène. Il en va à peu près de même avec le polystyrène, dont la dégradation par peroxydation par l'air à 80°C est notable.

Par contre l'ozonisation à froid n'entraine pas de dégradation et d'autant moins que l'ozonisation porte sur les noyeux benzéniques latéraux et non sur la chaîne principale.

Là encore, on peut atteindre des taux d'ozonisation beaucoup plus élevés ce qui permet la préparation de copolymères greffés à greffons très reapprochés jusqu'à 1 pour 5 segments styréniques ou au contraire très espacés.

En conclusion. Comme le professeur Natta je pense que l'on possède là une méthode de greffage intéressante et surtout si l'on sait fixer l'oxygène à froid mais le seul point où je me permettrai de ne pas être d'accord avec lui est celui où il affirme que cette méthode est supérieure aux autres car on connaît les résultats extrêmement intéressants obtenus par greffage par irradiation, transfert ou non terminaison.

H. Sack (*Paris*): Les résultats des essais mécaniques effectués sur ces greffés sont très intéressants. Par quelle méthode a-t-on moulé les éprouvettes de mesure? Sont el les homogènes et isotropes?

G. Natta (*Milan*): La courbe présentée par M. Lebel se réfère à l'oxydation du polyéthylène à l'ozone et elle est comparée avec nos données sur l'oxydation thermique du polypropylène qu'ils ont extrapolées.

Je voudrais mettre en relief à ce propos les grandes différences qui existent entre l'oxydabilité et dégradabilité du polyéthylène et du polypropylène, qui sont telles à rendre une telle comparaison très peu signifiante.

Le polypropylène, en effet, est bien plus sensible que le polyéthylène aux procédés de dépolymérization, comme on peut le constater en particulier dans l'emploi des méthodes de péroxydation et de réticulation basées sur l'irradiation.

Pourtant, les résultats obtenus avec le polyéthylène ne peuvent pas être directement étendus au polypropylène.

Les données reportées dans les epreuves correspondent a des echantillons qui ont été prepares par compression du polystyrène greffè sur les poly-α-olefines.