Some Peculiar Features of Radiation Grafting of Monomers of Various Structures and Reactivities onto Polyolefins

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ABSTRACT: Some peculiar features were studied for radiation grafting of monomers of various structures and reactivities in radical polymerization onto polyolefins (polyethylene and polypropylene). From the point of view of the kinetics and mechanism of grafting, the monomers are divided into two classes: The first class includes all monomers active in radical polymerization. When irradiated together with the polymeric matrix, they are grafted onto it as long polymeric chains and parallel to this occurs homopolymerization. The second class includes nonactive or slightly active monomers for radical polymerization. They are characterized by the formation of single units or short grafted chains. The possibility to add nonactive monomers with high radiation chemical yields was demonstrated. A mechanism was proposed to explain high radiation yields for a number of nonactive monomers by transferring the radical state along and/or between polymer macromolecules. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 711–718, 2000

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INTRODUCTION

The possibility to synthesize new polymers with various structures and properties is limited by the monomers available. For this reason, various processes for the modification of finished polymers become very important. Graft polymerization is one of the promising modern methods for the modification of polymers: It allows one to change the structures of the initial polymers and to add various functional groups to them. Among the methods of graft polymerization, a special place belongs to radiation graft polymerization. For at least 20 years, it has become a separate scientific direction of applied research.

Many articles have been devoted to various aspects of radiation graft polymerization.[1–9] The authors of these articles used well-known radical polymerization active monomers for graft polymerization, namely, styrene, acrylic, and methacrylic acids and their esters, acryl amide, acrylonitrile, vinyl pyridine, etc. These monomers can be grafted onto initial polymeric matrices by direct irradiation of the polymer and monomer (direct radiation graft polymerization) and by the contact of the monomer with preirradiated polymer in a vacuum, inert fluid, or air (postirradiation graft polymerization). In the case of graft polymerization, active monomers form long macromolecules grafted onto the polymeric matrix (MW is approximately 10^6): They can form their own supermolecular structure.[4] As a result of radiation graft polymerization, graft copolymers were prepared,

combining the properties of both initial and graft polymers. As a rule, a number of the properties of graft copolymers exceed those of the mechanical mixture of polymers.

At the same time, the literature data available do not describe the problem of radiation grafting of monomers which are nonactive or slightly active in radical polymerization [we call them non-homopolymerizable monomers (HNM)]. They include monomers of allyl groups, vinyl ethers, 1,2-disubstituted derivatives of ethylene,[10] vinyl alkoxy silanes (VS),[11] etc. These monomers do not tend to form long polymeric chains in radical processes (in the majority of cases, polymerization by ionizing irradiation, especially at room temperatures and low dose rates, is a radical process). At the same time, they are prone to reactive interaction with macroradicals of the initial polymer which brings about its modification. The aim of this article was to study the peculiar features of radiation grafting onto polyolefins (POs) of monomers of the HNM series.

EXPERIMENTAL

Dispersive nonstabilized isotactic polypropylene (PP) Daplen of Borealis (Linz, Austria) with an MFI of 0.3–0.5 and low-pressure polyethylene (LPPE) of 273-79 grade with a α-butene content of 0.5 mol % and an MFI of 0.30–0.50 were used as the initial polymers. The crystallinity degree of PP is 53% and the crystallinity degree of LPPE is 65%.

The following monomers were used:

vinyltrimethoxysilane (VTMS), pure grade	$T_{boil} = 122°C$ $d^{25} = 0.967$ g/cm^3
vinyltriethoxysilane (VTES), pure grade	$T_{boil} = 160.5°C$ $d^{25} = 0.905$ g/cm^3
monovinyl ester of ethylene glycol (MVEG), pure grade	$T_{boil} = 160°C$
vinyl butyl ether (VBE), pure grade	$T_{boil} = 93.8°C$ $d^{20} = 0.780$ g/cm^3
vinyl isobutyl ether (VIBE), pure grade	$T_{boil} = 83.3°C$ $d^{20} = 0.768$ g/cm^3
allyl acetate (AAc), pure grade	$T_{boil} = 103°C$ $d^{20} = 0.938$ g/cm^3
allyl trimethoxysilane (ATMS), pure grade	$T_{boil} = 146°C$ $d^{20} = 0.963$ g/cm^3
1,2,4-trivinylcyclohexane (TVCH)	$T_{boil} = 130°C$ $d^{20} = 0.948$ g/cm^3
maleic anhydride (MA), reagent grade	$T_{melt} = 52.8°C$ $d^{20} = 1.480$ g/cm^3
diisopropyl maleinate (DIPM),	$T_{boil} = 232°C$
pure grade	$d^{20} = 1.030$ g/cm^3
dibutyl maleinate (DBM), pure grade	$T_{boil} = 126°C$ at 5 mmHg $d^{20} = 0.982$ g/cm^3
styrene (St), pure grade	$T_{boil} = 104°C$ $d^{20} = 0.906$ g/cm^3
methacrylic acid (MMA), technical grade	$T_{boil} = 160.5°C$ $d^{20} = 1.015$ g/cm^3
α-methyl styrene (a-MST) pure grade	$T_{boil} = 161°C$ $d^{20} = 0.913$ g/cm^3

Stabilized monomers were isolated from inhibitors by vacuum-distillation.

Monomer grafting or graft polymerization was carried out by simultaneous irradiation of the polymer and monomer with γ-rays of the Co^{60} isotope. Five grams of the PO powder was charged into the ampule, the ampule was connected to a vacuum pump, and air was evacuated to $1–10^{-1}$ mmHg. Then, the ampule was cooled in a Dewar flask containing ice and 1.5–2 mL of the monomer was syringed into the ampule (a laboratory px-γ-30 unit was used for irradiation). The dose rate of 0.3 Mrad/h was used. When nonactive monomers were used, before irradiation, the monomer was sorbed by the polymer by thermostating the ampule with the polymer and monomer at 100–140°C for 30 min. To decrease the yield of the nongrafted polymer, active monomers were used as acetone solutions. After γ-irradiation, the ampules with the polymer were opened and the modified polymer was washed on a filter by a solvent to remove the nonreacted monomer. In the case of active monomers, nongrafted polymer was extracted in a Soxhlet apparatus. Then, the samples were dried in a thermovacuum cabinet at 100–140°C to a constant weight. The content of the graft monomers was determined by IR Fourier transform spectroscopy, using a Perkin–Elmer spectrometer Model 1150, by integral intensity of the band group in the range of characteristic vibrations of functional groups. The apparatus was calibrated for the quantitative determination. Films, 10–200 μm, were used for the IR studies prepared from dispersive copolymers by hot-compression molding. When the content of the comonomers in POs was 0.01–2 mol/kg, the accuracy of the determination amounted to 5% rel.

The sorption characteristics of polymer–monomer pairs were studied using PP and LPPE film models. The film thickness was selected as equivalent to the size of the dispersive particles of POs (S_{sp} approximately 4×10^{-2} m^2/g). The monomer

Table I   Results of Direct Radiation Grafting of Monomers onto POs (Absorbed Dose, 2 Mrad)

Monomer	Amount of Sorbed Monomer (mol/kg)		Grafting Degree (mol/kg C)		Radiation Chemistry Yield (G_g)[a]	
	In PP[b]	In LPPE[c]	In PP	In LPPE	In PP	In LPPE
Homo-nonpolymerizable monomers						
VTMS	0.35	0.39	0.39	0.42	196	211
VTES	0.41	0.45	0.58	0.62	291	311
MVEG	0.30	0.34	0.62	0.15	311	753
VBE	0.22	0.25	0.12	0.60	60	301
VIBE	0.18	0.30	0.13	0.35	65	176
AAc	0.15	0.18	0.03	0.04	15	20
ATMS	0.28	0.31	0.02	0.06	10	30
TVCH	0.31	0.41	0.01	0.013	5	6.5
MA		Below 0.01	0.03	0.03	15	15
DIPM	0.30	0.27	0.025	0.06	13	30
DIBM	0.38	0.35	0.03	0.08	15	40
Homopolymerizable monomers						
St	0.16	0.33	1.2	2.5	602	1254
MAA	0.26	0.35	1.3	2.7	652	1354
α-MSt	0.16	0.59	0.02	0.16	10	80

[a] No. molecules of the graft monomer for 100 eV absorbed energy with $G_{gr} = CN_A/D100$, where C is grafting degree (mol/kg). NA, Avogadro's no.; D, absorbed dose (eV/kg).
[b] 30 min at 140°C.
[c] 30 min at 100°C.

content of the film was determined by IRS spectroscopy.

Using radio spectrometry, the concentration of the free radicals of the irradiated polymers was determined by EPR of the Rubin type (wavelength λ = 3.2 cm) at room temperature. The concentration of radicals was determined from the ratio of areas of the spectra of the radical and reference; the areas were obtained by double graphical integration of the first derivatives of the EPR spectra. The EPR line of the Cr^{3+} ion in the rubin crystal in the spectrometer resonator together with the sample to be studied was used as a reference of intensity.

The structure of copolymers was studied by ^{13}C-NMR spectroscopy. An NMR Fourier spectrometer of B567A type of the Tecla Co. at 25 MHz and an NMR spectrometer of the Bruker AN-500 Co. at 125 MHz at 140°C were used. The polymers were dissolved in o-dichlorobenzene. D-n-dichlorobenzene was used as a signal source for deuterium with 20 vol % of it added to the solvent.

RESULTS AND DISCUSSION

Table I shows the experimental results of the study of grafting of monomers of various activities onto PO by cooperative γ-irradiation of monomers with PP and LPPE. The data for radiation grafting polymerization of active monomers (St and MAA) are shown only for comparison with those for radiation grafting of HNM. We do not discuss them in detail because it is not the aim of our study. We draw your attention only to the fact that radiation graft polymerization is characterized by high radiation chemical yields G_{gr}: They are defined by the nature of the monomer and polymer matrix. The scheme of the graft polymerization of active monomers is as follows:
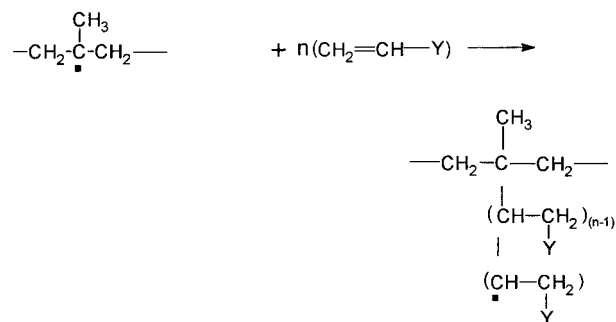
In contrast to active monomers, the G_{gr}'s of HNM are considered to be different. They vary
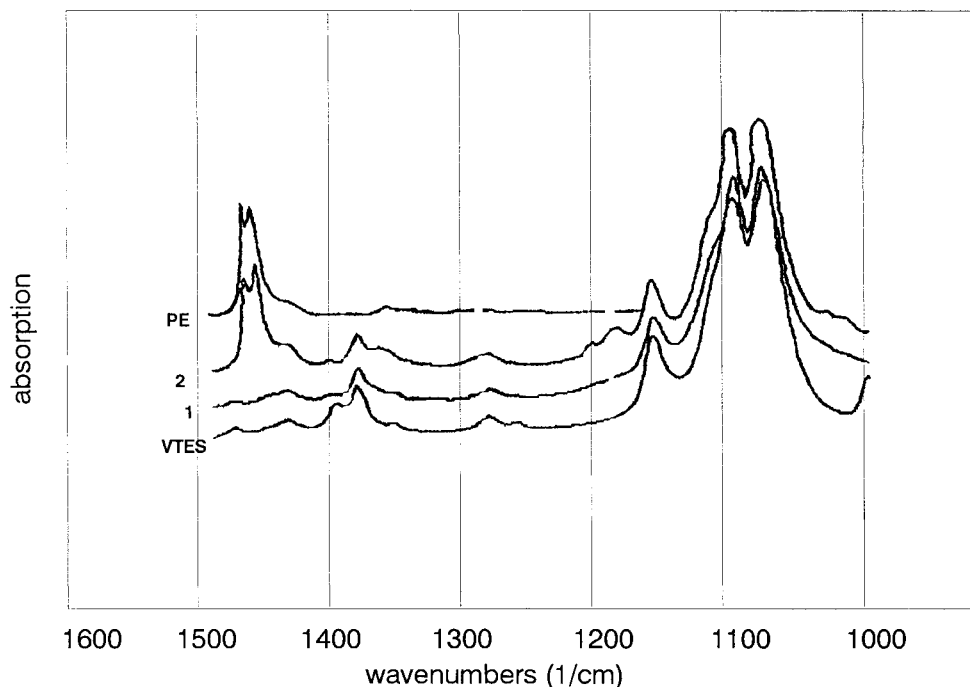
Figure 1 IR spectrum of linear PE with (1) radiation-grafted VTES and (2) irradiated VTES. Absorbed dose, 2 Mrad. The spectra of the initial PE and VTES are shown for comparison.

from single-molecule grafts to several hundreds. Probably, the activity of monomers in the process of radiation grafting is defined by the following factors:

- reactivity of the monomer and radical formed by it;
- sorption–diffusion properties of the monomer–polymer pair;
- conditions of radiation irradiation (dose rate, absorbed dose, irradiation temperature).

Radiation irradiation of all the polymer–monomer pairs studied was carried out under identical conditions. The insignificant differences in the quantities of the sorbed monomers for identical periods of time (excluding MA) indicate that the sorption–diffusion properties of the polymer–monomer pairs considered are close. We suppose that significant (more than 100 times) differences of the G_{gr} of the monomers considered are explained mainly by their chemical structures.

In the case of radiation irradiation of polymer–HNM systems, reactive free radicals are formed in the polymer and in the monomer. Macroradicals of the polymer can be deactivated by recom-

bination with each other or by recombination with the radical of the monomer. The latter event is more probable because low molecular monomers and their radicals have higher mobility than macroradicals. Supposing that every meeting of the macroradical and HNM brings about an interaction, that is, monomer grafting, then the radiation–chemical yield of grafting G_{gr} is equal to that (G_R) of the free radicals of PO.[12] Practically, G_{gr} can be even lower than G_R because not all macroradicals react with the monomer. Thus, after radiation irradiation of PP in the presence of VTES-fixed 10^{17} residual radicals of PP/g persisted in the copolymer sample, they probably did not react with vinyl silane due to their insufficient availability. Our data (Table I) shows that G_{gr} exceeds G_R; for some HNM, it exceeds it 100 times. This feature can be explained by the fact that HNM is grafted in the form of long chains, as in the case of active monomers, or grafting is increased by radical transfer processes from the HNM to the PO main chain.

The studies of the structure of the copolymers of PO and HNM by IR and NMR spectroscopy have shown that HNM is grafted in the form of single units. Let us consider the struc-
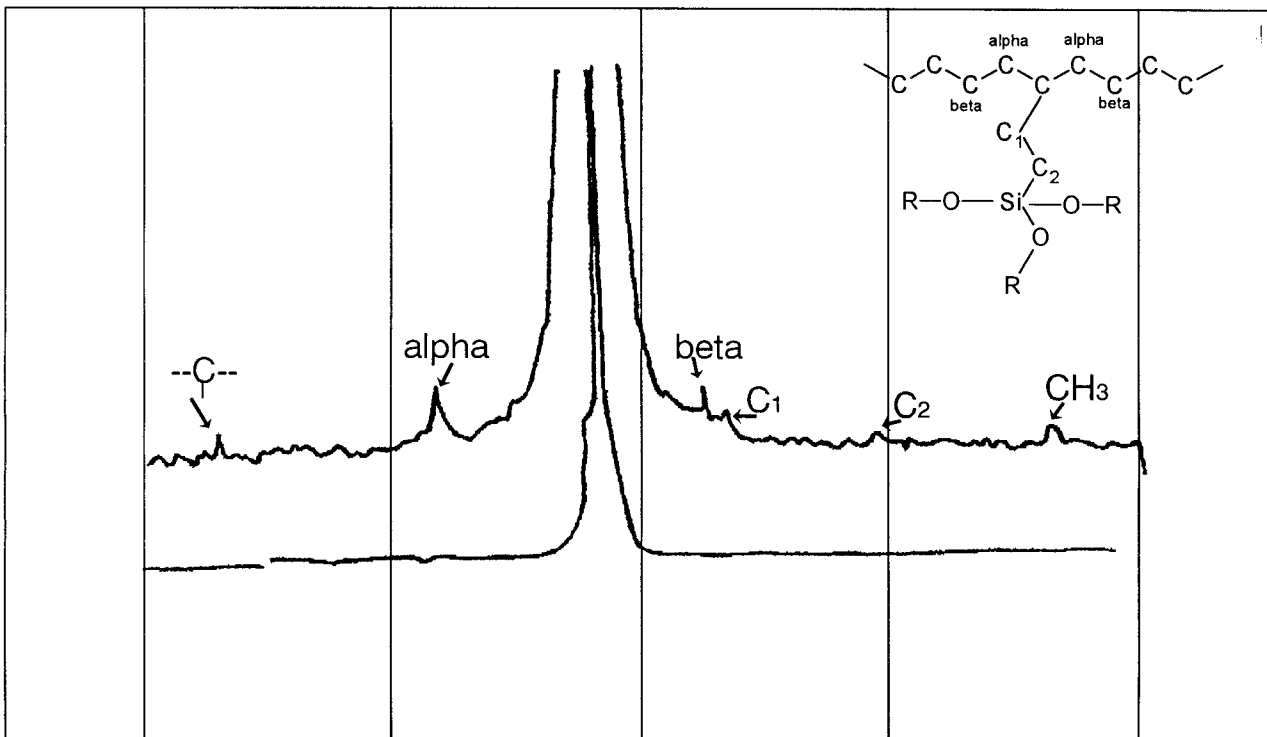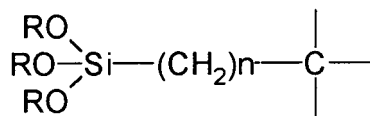
Figure 2 ^{13}C-NMR spectrum of LPPE with radiation-grafted VTES.

ture of PO with grafted VTES in more detail (Figs. 1 and 2).

For convenient interpretation, high molecular polyethylene (LPPE) was used as a model in the consideration of the IR spectra: It allowed us to separate spectrum bands which appeared as a result of grafting. The study of the IR spectra of irradiated VTES and LPPE with grafted VTES (Fig. 1) showed, first, that VTES did not give a typical homopolymer and some addition of monomers occurred, possibly with the formation of cycles, and, second, in case when VTES was grafted onto the polymer, two narrow bands were observed in the range of 1200 cm^{-1}, which can belong to structures of the type

$$\begin{array}{c} RO \\ RO\!-\!Si\!-\!(CH_2)n\!-\!C\!- \\ RO \end{array}$$

n = 2 or 3

It confirms the grafting of VS as a single unit. This type of grafting was confirmed by ^{13}C-NMR data. Figure 2 shows the NMR spectrum of LPPE with grafted VTES (VTES content is 2 mol %). This spectrum is a typical spectrum for LPPE containing some side branches in the molecules. In other words, this spectrum contains one intensive line relevant to carbons of PE chains and, in addition, it also contains weak lines of tertiary carbon, α- and β-carbons located in the main chain on both sides of tertiary carbon and lines of carbons of side branching. The lines of the spectrum of grafted PE are identified on the basis of comparison of this spectrum with those of copolymers of ethylene with α-olefins and that of silane. All the above show that the addition of VTES to LPPE is carried out as short side branches consisting of one molecule of silane.

Unfortunately, the NMR spectra of PP with grafted VTES are less informative. Only three bands were observed in the ^{13}C-NMR spectrum of isotactic PP referring to primary, secondary, and tertiary atoms of carbon. However, actual PP spectra included some low intensive associated bands in addition to the above three main bands after washing the atactic fraction with hot heptane. The associated bands correspond to structures with a normal addition of propylene units.

We failed to separate bands relevant to the units of the VTES addition to the polymer chain in the spectra of PP with grafted VTES. At the same time, carbon atoms of ethoxy groups were evident. One of the possible explanations of this feature is the accidental addition of VTES to any carbon of the PP chain (primary, secondary, or tertiary ones). It does not contradict the data obtained from the studies of the IR spectra. Experiments have also demonstrated that all the other HNM considered do not polymerize by radiation irradiation in the range of doses much higher than the one used.

The above data allow us to propose a chain mechanism of grafting with the transfer of the radical state on the polymer for HNM with high G_{gr}. This mechanism is as follows:
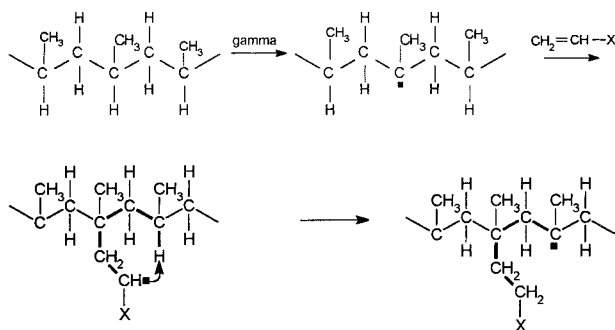

The idea of a similar process is as follows: —CH$_2$—ĊH—X The grafted monomeric radical has the role of the acceptor of the hydrogen atom by breaking it off the polymer: The probability of breaking off a hydrogen atom from the polymer is high because the polymer concentration is many times higher than that of the sorbed monomer. As a result of breaking off the hydrogen atom, a new radical site is formed on the polymer which initiates grafting. We suppose that the transfer of the radical state is possible not only along one polymer macromolecule but also between macromolecules. Break-off of the chain, for transfer of the radical state to stop grafting, can take place in the case of recombination of two macroradicals at the expense of inter- or intramolecular migration of the radical state.[13] This recombination is difficult because macroradicals are located far from each other. Thus, the amount of macroradicals 10^{18} pcs/g (number of radicals formed by 2 Mrad irradiation) relates to one radical for 4000 units of propylene or 6000 units of ethylene.

The proposed chain mechanism of grafting is clearly shown for VTMS, VTES, MVEG, VBE, and

VIBE monomers which do not form stabilized radicals. The above HNM are grafted with high probability, not statistically but by "nests," because the transfer of the radical state is possible by breaking off hydrogen atoms of the monomer close to the radical. Grafting by "nests" is confirmed by the fact that practically all OH groups are in the form of associates and not in the form of free groups in the IR spectra of grafted MVEG.

In the case of the grafting of allyl monomers (AAc, ATMS, TVCG), intensive development of the chain process with the transfer of the radical state onto the polymer does not take place. When the allyl monomer and PO are irradiated, the graft radical of the monomer —CH$_2$—ĊH-CH$_2$—Z breaks off hydrogen atoms not from the polymer but from its own monomer with a weak allyl C—H bond (the break energy of the allyl bond CH$_2$=CH—CH$_2$ ΔH is 77 kcal/mol, while the break energy of the bond C$_3$H$_5$ ΔH is 95 kcal/mol[14]) with higher probability. In this case, the allyl radical formed has high resonance stability[10]:
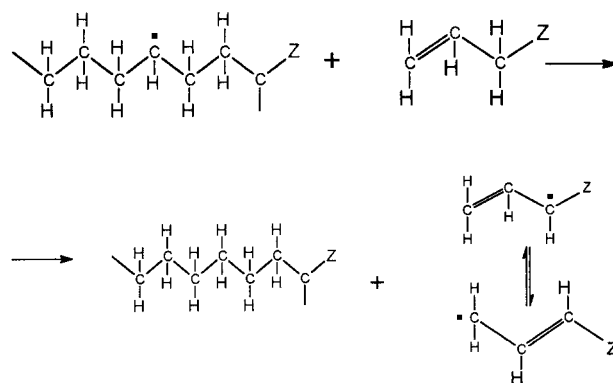
At the same time, allyl monomers do not tend to form homopolymers (well-known autoinhibition of allyl monomers is related to the above chain transfer to the monomer[10]). For this reason, in the case of radiation irradiation of polymers together with allyl monomers, the grafting degrees of monomers and, respectively, G_{gr} are low (Table I). Radiation grafting of 1,2-disubstituted derivatives of ethylene to PO are also characterized by low G_{gr}. MA and maleates (DIPM and DIBM) belong to them. The chain propagation in homopolymerization of 1,2-disubstituted derivatives of ethylene is known[10] to be difficult due to steric hindrance of the addition of the monomers to the propagating radical. Thus, the extensive polymerization of MA by radiation irradiation is observed only at high absorbed doses above 20

Mrad.[15] We suppose that the steric factors also prevent us from radiation grafting MA and maleates by a chain mechanism (an insignificant sorption degree of MA to PO can hardly become the only reason for a low grafting degree, because, in case of maleates, it is also low although they are sorbed in PO similar to many other monomers considered—Table I).

A specific place among the monomers considered belongs to α-methyl styrene, which is included in the class of 1,1-disubstituted derivatives of ethylene. Due to the effect of two substituents at the carbon of the vinyl group, compared to many vinyl monomers, this monomer is characterized by low enthalpy of polymerization ($\Delta H = -8.4$ kcal/mol) and low ultimate polymerization temperature (T_{cr}); above this temperature, depolymerization prevails. Thus, it is known[16] that, at the equilibrium concentration $[M]_{cr}$ of α-MSt at 1, mol/L, T_{cr} is equal to 6°C. The highest concentrations of α-MSt sorbed by PP and LPPE before γ-irradiation are equal to 0.17 and 0.63 mol/L, respectively. Thus, for thermodynamic reasons, radiation graft polymerization of α-MSt cannot be carried out at room temperature as it was in our case. Low G_{gr} for the PP–α-MSt pair indicates that grafting of α-MSt onto PP as single units by a chain mechanism is also not realized. This feature can be explained by stabilization of the α-MSt radical grafted onto PP at the expense of conjugation with the aromatic ring:
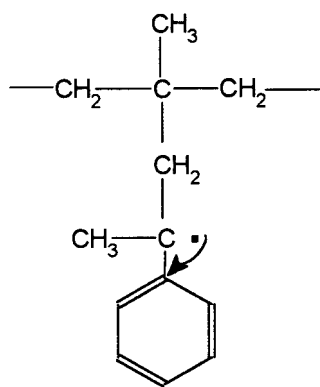
The experimental results obtained are not sufficient to explain why, in the case of grafting α-MSt onto LPPE, G_{gr} is eight times higher than in the case of grafting onto PP (Table I). The explanation of this fact requires further studies. We draw your attention to the fact that, for all HNM considered, G_{gr} is higher for LPPE than that for PP. It is apparent not only for α-MSt but also for vinyl

ethers. It is possible that the above feature can be explained by some difference of sorption values of the monomers before γ-irradiation.

It is necessary to take into account that sorption–diffusion properties of polymer–monomer pairs can be changed significantly in radiation irradiation.[6] The latter is confirmed by the fact that grafting degrees of HNM obtained are higher than their sorption in some cases (Table I).

Thus, from our point of view, the mechanism of the interaction of the monomer and polymer, when they are irradiated together, is defined mainly by the activity of the monomer and its radical. In the case of homopolymerizing monomer graft polymerization is carried out, whereas in the case of HNM single units (or possibly very short chains) are grafted.

HNM forming nonstabilized and sterical nonhindered radicals is grafted by a chain mechanism with the transfer of the radical state onto the polymer. Due to the chain mechanism, these monomers can be added to the polymer in significant amounts at small irradiation doses. As a result of the chain mechanism of radiation grafting, the units of grafted monomers are distributed in the polymer by "nests" and not statistically. Thus, by studying the chemical structure of the monomer, it is possible to predict the results of its radiation grafting onto the polymer.

CONCLUSIONS

The γ-irradiation grafting of monomers with various structures onto PE and PP under identical conditions was investigated. The results show differences in the grafting degrees as well as of the radiation chemistry yields of the HNM and the homopolymerizable monomers. Nevertheless, without MA, the amount of the sorbed monomers are in the same order of magnitude. The grafting degrees C of all the monomers correlate with the radiation chemistry yield G_{gr}, but the homopolymerizable monomers St and MMA are expected to have a one-to-two orders of magnitude higher one than that of the HNMs.

Of special interest are the differences in the HNMs which exceed 10–100 times. This feature can be explained only by a radical transfer process from the higher reactive HNMs to the PO main chain, because the structure of the grafted HNM shows only single units. So, we conclude that VTMS, VTES, and MVED have high transfer

rates, while the transfer rates of AAG, ATMS, TVCH, and the maleates are relatively low.

It could be shown that the HNMs with high transfer rates led to a high concentration of these monomers in the surroundings of the first addition step by intramolecular transfer reactions at the PO main chain, the so-called nests, and not to a statistical distribution. The irradiation of the allyl monomers leads preferably to the formation of high resonance stable allyl radicals which cannot break off hydrogen atoms from the PO chain. The termination reaction of the allyl radicals are preferred and low grafting degrees follow.

The well-known high transfer rate of MA could not be found because of its low amount of sorption. These results are in correlation with the theory of radical processes with different monomers. The low grafting degree of α-MSt can be explained by stabilization of the α-MSt radical grafted onto PP. The C and G_{gr} of all monomers in LPPE in comparison to i-PP can be explained with the better sorption–diffusion properties and the better interactions of the polymer–monomer pairs in LPPE.

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