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G. NATTA, F. SEVERINI, M. PEGORARO, and C. TAVAZZANI

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From the Istituto di Chimica Industriale del Politecnico, Milano/Italy,
and Centro Ricerche Milano Società "Montecatini Edison"

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SUMMARY:

The polymerization of methyl acrylate in an atactic polypropylene solution in the presence of radical initiators (benzoylperoxide, *tert*-butylperpivalate, α.α′-azoisobutyronitrile, lauroylperoxide) yields a mixture of grafted polymethylacrylate/polypropylene copolymer and of a methyl acrylate homopolymer.

The crude polymers are fractionated and the influence of the concentration of both monomer and initiator, and of the type of solvent used on the percentage of grafting was studied.

The concentration of active macroradicals in the grafting reaction is measured with the help of a simplified kinetic scheme.

ZUSAMMENFASSUNG:

Die Polymerisation von Acrylsäuremethylester in einer Lösung von ataktischem Polypropylen mit radikalbildenden Initiatoren (Benzoylperoxid, Perpivalinsäure-*tert*-butylester, Azoisobuttersäuredinitril, Lauroylperoxid) ergibt eine Mischung von Acrylsäuremethylester/Polypropylen-Pfropfcopolymeren und von homopolymerem Acrylsäuremethylester.

Die rohen Polymeren wurden fraktioniert, und der Einfluß der Konzentration der beiden Monomeren, des Initiators und der Art des Lösungsmittels auf das Ausmaß der Pfropfungsreaktion wurde untersucht.

Die Konzentration der aktiven Makroradikale bei der Pfropfungsreaktion wird an Hand eines vereinfachten kinetischen Schemas abgeschätzt.

Introduction

In a previous paper[1] we summarized the results obtained in graft polymerization processes carried out using hydroperoxidic derivatives of crystalline or amorphous poly-α-olefins, as initiators.

The results obtained indicated that the reaction products may be used to prepare materials differing, by their properties, from the initial poly-α-olefins. In particular, it is possible to obtain products that may be conveniently used as high-impact materials, adhesives, paints, *etc.* Analogous results were also obtained by other methods of grafting, *e.g.* by chain transfer.

This communication describes the graft polymerization of methyl acrylate on atactic polypropylene in the presence of low-molecular-weight initiators, acting as chain transfer agents. The graft reaction may be initiated both by the action of primary radicals deriving from the decomposition of the initiator and by the reaction of polypropylene molecule with the growing polymeric chains of methyl polyacrylate. The system is particularly suitable for the study of the kinetics of the reaction; actually, if a convenient solvent is employed, it is possible to operate in homogeneous phase.

The graft reaction, carried out in benzene solution, as it was accomplished by other authors[2], takes place with good transformation yields of the reagents into graft copolymers.

Graft Polymerization by Chain Transfer

As it is well known, the free radicals may remove an atom from a preformed polymeric chain, with formation of a radical acting as a site of attack for the monomer to be grafted[3]. The point of attack may be located either on the lateral groups of the chain, or on the chain itself. The initial free radicals generally derive from the decomposition of an initiator, or they are growing chains.

The scheme of the reactions of opening and of propagation, which may be adopted to a first approximation, is in our case as follows:

$$R_2 \rightarrow 2R\bullet \tag{1}$$

$$R\bullet + M \rightarrow RM\bullet \tag{2}$$

$$RM\bullet + nM \rightarrow RM_nM\bullet \tag{3}$$

$$R\bullet + SH \rightarrow RH + S\bullet \tag{4a}$$

$$RM_n^{\bullet} + SH \rightarrow RM_nH + S\bullet \tag{4b}$$

$$S\bullet + nM \rightarrow SM_{n-1}M\bullet \tag{5}$$

Reactions (1), (2), (3) respectively correspond to the decomposition of the initiator with formation of primary radicals, to the addition of a first monomeric unit to these primary radicals, and to the growth of the homopolymeric chain by subsequent addition of the monomer molecules.

In reactions (4a), (4b) a hydrogen atom of the main polymeric chain is removed by the action of either a primary radical $R^{\bullet}$ (reaction (4a)) or of a growing molecule (reaction (4b)).

Finally, reaction (5) represents the addition of the monomer to the active center and the formation of a graft copolymer.

At an early stage of research, graft copolymers were supposed to derive exclusively from reaction (4b); in fact, in the competition between monomers and main chain, the reaction of the primary radicals with a vinyl monomer (reaction (2)) was considered easier than the removal of a hydrogen atom from a macromolecule (chain transfer to polymer). This hypothesis was supported by the fact that the activation energy for a chain transfer reaction is higher than for the addition of a monomer.

However, more recent experiments[4] demonstrated that reaction (4a) cannot be excluded and that for some polymer-monomer systems, grafting may or may not occur, depending on the nature of the initiator[5], *i.e.* of the primary radicals obtained from its decomposition; on the contrary, other systems are not sensitive to the nature of the initiator. A typical example is the polymerization of methylmethacrylate in the presence of polystyrene; appreciable yields of graft copolymer are obtained only with the use of benzoyl peroxide as an initiator. Instead, with $\alpha.\alpha'$-azoisobutyronitrile (AIBN) or di-*tert*-butyl peroxide (DTBP) grafting is negligible. In contrast with it, the formation of graft copolymers of vinyl acetate with polymethylmethacrylate does not depend on the type of initiator.

The frequency of reactions (4a) and (4b) with respect to the frequency of reactions (2) and (3) depends on the competition between the rates of growth and of transfer. This competition is characterized by the value of the constant of transfer of the monomer, defined as the ratio between its rate-constant of transfer and its rate-constant of propagation. The constant of transfer depends on the nature of the reacting macroradicals and of the transfer agent.

As shown by a previous investigation, chain branching and grafting increase with increasing both temperature and polymer concentration[6]. The reaction of chain transfer may be facilitated by functional groups having a high degree of reactivity, on the polymer to be grafted[7].

With regard to reaction (5), a few experiments[6] seem to indicate that the monomer addition to the macroradicals produced by chain transfer depends directly on the reactivity and polarity of both radical and monomer.

Reactive groups sensitive to the attack of free radicals may be functional side groups of the macromolecules. This fact was early shown by grafting experiments of ethylene on polyvinylacetate in a benzene solution in the presence of diethylperoxide[8], and of methylmethacrylate and vinylacetate[9] on polyvinylbenzoate. Also mercaptanic[10] and bromomethyl groups[11] are particularly active in the reactions.

Grafting by chain transfer was accomplished not only in homogeneous mediums, but also using emulsion polymerization techniques, *i.e.* by polymerization of the monomer to be grafted in the presence of an aqueous emulsion that contains the polymer employed as backbone[12,13,14].

Reaction of Grafting – a Simplified Scheme

The grafting reaction of vinyl monomers on a polyhydrocarbon such as polypropylene or on ethylene-propylene copolymers containing tertiary carbon atoms, preferably occurs on these tertiary sites. In fact, the reactivity of aliphatic hydrogen with respect to different radicals, in the reaction:

$$X\bullet + SH \xrightarrow{k_{tr}} XH + S\bullet \qquad (a)$$

is higher when hydrogen is bound to a tertiary carbon atom, independently of the type of radical X•.

The complete kinetic scheme of the grafting reaction, taking also into account the simultaneous occurrence of homopolymerization reactions, is very complex.

We limited our study to the reactions leading to formation of the grafted polymer, by supposing that free radicals X• are already present in the system.

Reaction (a) producing the active centres S• on the hydrocarbon polymer chain (backbone) is the step preceding grafting.

In reaction (a) the radical X• may be either a free radical (*e.g.* RO•) directly derived from the decomposition of the initiator (*e.g.* a RO–OR peroxide), or else a radical consisting of the active monomer M• or of a homopolymeric radical (*e.g.* ROM_{n-1}–M• hereinafter indicated by O•) or of a grafted one ($S–M_{n-1}M\bullet$), all radicals ending by M•, when the solvent is inactive.

It is followed by a series of propagation reactions and by the termination reaction:

$$SM_n^{\bullet} + Y\bullet \xrightarrow{k_t} P \text{ or } 2P \qquad (6)$$

that is one or two inert polymeric products, one at least being a grafted polymeric chain.

By a single coupling, only one macromolecule P is obtained, while by disproportionation two macromolecules are obtained.

In reaction (6), the radical Y• may be whatever radical present in the system (*e.g.* RO•, O•, SM_{n-1} M•).

Practically no crosslinking reactions have been observed under our experimental conditions; therefore when $Y\bullet = SM_{n-1}M\bullet$, reaction (6) is supposed to occur only by disproportionation.

Grafted polymeric macroradicals may terminate also by transfer with a substance T capable of transfer.

$$SM_n^\bullet + T \xrightarrow{k_{tr}} SM_n + T\bullet \tag{7}$$

T may be the homopolymer, the grafted polymer or the polymeric support SH, the monomer M, the solvent.

The rate of the reaction of grafting r_i, which indicates the mole number of monomer consumed during grafting per unity of time and of volume of the system, is

$$r_i = -d[M]_i/dt = k_p[S\bullet][M] \tag{8}$$

where [S•] indicates the concentration of the grafted growing macroradicals.

S• is assumed to be equivalent to $SM_n^\bullet$ and the index "i" indicates the reaction of grafting.

The rate of the termination reaction r_{ci}, which determines the number of moles of grafted chains produced per unity of time and of volume of the system, is given by:

$$r_{ci} = k_t[S\bullet][Y\bullet] + k_{tr}[S\bullet][T] = [S\bullet] \cdot \{k_t[Y\bullet] + k_{tr}[T]\} \tag{9}$$

Between time t and t + dt, the increase in weight (per volume unit) of the polymeric system, due to the grafting reaction only, is given by the following expression.

$$(dP)_i = mr_i\,dt + m\bar{x}_0\,r_{c,i,a}\,dt \tag{10}$$

where "m" is the molecular weight of the monomer, $\bar{x}_0$ the average degree of polymerization of a homopolymeric macroradical O•, $r_{c,i,a}$ the rate of termination by coupling of S• with O•.

This equation not only takes into account the reaction of propagation, but also the fact that, within the time mentioned above, a weight increase may occur from the coupling of radical S• or $SM_n^\bullet$ with a radical O•, which already has an average degree of polymerization $\bar{x}_0$.

This last reaction occurs with a rate

$$r_{c,i,a} = k_{t,a}[S\bullet][O\bullet] \tag{11}$$

By integrating (10), we obtain

$$\Delta P/m = \int_0^t [S\bullet]\,\{k_p[M] + k_{t,a}\,\bar{x}_0[O\bullet]\}dt =$$

$$\int_0^t [S\bullet]\,k_p[M]\left\{1 + \frac{k_{t,a}\bar{x}_0[O\bullet]}{k_p[M]}\right\}dt \simeq \int_0^t [S\bullet]\,k_p[M]\,dt \qquad (12)$$

which is valid if the fractional term between brackets may be considered small with respect to unity, as it occurs in practice.

It follows that the increase in weight due to the grafting reaction essentially depends on the concentration of the active centres S• present on the polymer chains to be grafted, as well as on the concentration of the monomer and on its nature (k_p).

In theory, the concentration [S•] may be expressed as a function of the quantities characterizing the system from a kinetic point of view (*i.e.* concentration of the initiator, and kinetic constants of the various reactions), by writing as many steadystate equations as are the types of radicals present in this system.

However, solving these equations is of extreme difficulty.

Quantitatively, [S•] is a function of the concentration of the primary radicals, and of the other radicals capable of removing hydrogen from the backbone chain, such as M•, $SM_n^\bullet$, O•.

Experimentally, according to Eq. (8), the value of [S•] may be replaced by the following formula:

$$[S\bullet] = r_i/k_p[M] \qquad (13)$$

The equation may be normalized into

$$[S\bullet] = \frac{\frac{r_i}{G}Vm}{k_p\frac{[M]Vm}{G}} \simeq \frac{\frac{d}{dt}\frac{Q}{G}}{k_p\frac{B}{G}} \qquad (14)$$

where V is the volume of the system, G the weight of the polymer to be grafted initially present in the system, B the weight of the unreacted monomer present in the system at the time t, Q the weight of the monomer already grafted present in the system at time t.

Eq. (14) represents a good approximation when $\bar{x}_0 r_{c,i,a}$ is negligible with respect to r_i; its usefulness lies in the easy utilization of the analytical data.

Experimental Part

Materials used

Amorphous polypropylene consisted of the ethyl ether soluble fraction of a crude polypropylene obtained with propene, $TiCl_3$ and $Al(C_2H_5)_3$; its intrinsic viscosity determined in toluene at 30 °C was $0.4 \cdot 10^2$ cm³/g.

Initiators: Benzoyl peroxide (Bz_2O_2) purified by recrystallization of the commercial product of Carlo Erba, with a degree of purity of 99%. *tert*-Butylperpivalate (TBPV) with a content of 75%. Lauroyl peroxide (Laurox) with a 98% content, of Noury and Van der Lande. α.α′-azoisobutyronitrile (AIBN), a commercial product of Fluka.

Monomer: Methyl acrylate (AcMe) of BDH-made free of stabilizer by washing it with an dilute alkaline solution, and subsequently distd. under reduced pressure.

Solvents: Acetone, benzene, chloroform, cyclohexane, *n*-hexane, cumene: R.P. products of Carlo Erba.

Celite: 535, of Mascia e Brunelli Co.

Reaction of grafting

We used solutions of the polymer in the solvent indicated; the initiator was added while the mixture was kept under stirring; then the monomer used for grafting was added dropwise.

Grafting was carried out in sealed glass vessels under a practically pure nitrogen atmosphere; vessels were kept in slow motion in a thermostated bath of vaseline oil.

Other runs were carried out, always under nitrogen atmosphere, in a flask dipped into a thermostatic bath, while the reaction mixture was stirred at a constant rate.

The amount of methyl acrylate monomer that was not converted into grafted polymer or into homopolymer was determined by gas-chromatography using a 2 m column at 20% of β.β′-oxydipropionitrile on chromosorb W at 70 °C.

From the result obtained we were able to calculate the amount of monomer reacted. The fraction of monomer converted into grafted polymer was determined according to the methods described hereinafter.

Fractionation of the crude polymerisate and determination of the methyl acrylate content of the graft copolymer

The crude polymerisate was precipitated in an excess of methanol and the precipitate obtained was purified from ungrafted polymethylacrylate homopolymer by repeated washing with boiling acetone. The residue was dried under reduced pressure and subsequently analysed to determine the content of grafted monomer.

In many cases, the homopolymer was removed from the grafted product by dispersion of the crude reaction product (in solution) on celite, drying, and then percolating acetone. The extraction of the homopolymer being completed, the polymeric residue was extracted with benzene.

The amount of grafted methylacrylate units was determined either by saponification, with alcoholic KOH in excess, of the product dissolved in technical xylene, or by IR analysis, using for analytical purposes the ratio between the band at 5.75 μ of polymethylacrylate and that at 7.3 μ of polypropylene; calibration was carried out with mixtures – of known composition – of polypropylene and polymethylacrylate homopolymers.

Results

All runs were carried out using a 12 % solution of amorphous polypropylene in benzene. In all runs, the percent amounts of monomer and of initiator are expressed in grams per 100 g of polypropylene.

Table 1 summarises the results obtained by heating to 70 °C for 18 hrs methyl acrylate in a solution of polypropylene in benzene in the presence

Table 1. Polymerization of methyl acrylate in a solution of amorphous polypropylene in benzene. Temperature 70 °C; time 18 hrs; 50 g of a 12 % benzene solution of polypropylene; AcMe = 1.8 g; % Bz_2O_2 indicated in the table

% Initiator:	1	2	4	6
% methyl acrylate in the product residue to the acetonic washing:	13	14	16	13.1

of variable amounts of benzoyl peroxide. The monomer that was initially allowed to react was 30 % with respect to the polypropylene present; under our conditions it was almost entirely converted into grafted polymer and homopolymer.

As may be seen, the percentage of initiator has little influence on the content of methyl acrylate units present in the final grafted product.

Table 2 summarizes the results obtained by heating the same reaction mixture to 70 °C for 18 hrs in the presence of equimolecular amounts of different initiators

Table 2. Polymerization of methyl acrylate in a 12 % solution of amorphous polypropylene in benzene. Temperature = 70 °C; time 18 hrs; 50 g of a benzene solution of polypropylene; AcMe = 1.8 g; initiators = 0.00825 mole-%

Initiator:	Bz_2O_2	AIBN	Laurox	TBPV
% methyl acrylate in the product residue to the acetonic washing:	14	9	8.5	13.5

The data we obtained indicate that grafting is not negligible even by operating in the presence of AIBN; in this case, owing to the properties of this initiator[15], the reaction of grafting might be entirely attributed to chain transfer phenomena taking place between the growing homopolymer and the polypropylene present.

The influence of the solvent on the amount of grafted monomer was studied by using polypropylene solutions in different solvents. The results of Table 3 show that the percentage of grafting varies with the constant of transfer solvent-polymethylacrylate radical.

The amount of methyl acrylate present in the grafted product varies considerably with the amount of monomer which was initially allowed to react, for monomer concentrations up to 40 %; on the contrary, for higher concentrations, further variation becomes negligible.

The results obtained are summarized in graph 1. Fig. 2 shows plots *vs.* time of the amount of methyl acrylate actually grafted on polypropylene

Table 3. Polymerization of methyl acrylate in a 12 % solution of amorphous polypropylene in the solvents indicated. T = 70 °C; time = 18 hrs; AcMe = 30%; Bz_2O_2 = 2%; solution = 50 g; AcMe = 1.8 g

Solvent	% methyl acrylate in the residue to acetone washing	$C_s \cdot 10^4$ constant of transfer at 80 °C
n-Hexane	13	
Cyclohexane	13	12
Benzene	14	4.5
Cumene	4.3	16.2

(Q/G) and the actual ratio of monomer present to polypropylene (B/G), for a reaction carried out at 70 °C, using a mixture of initial composition shown in the figure.

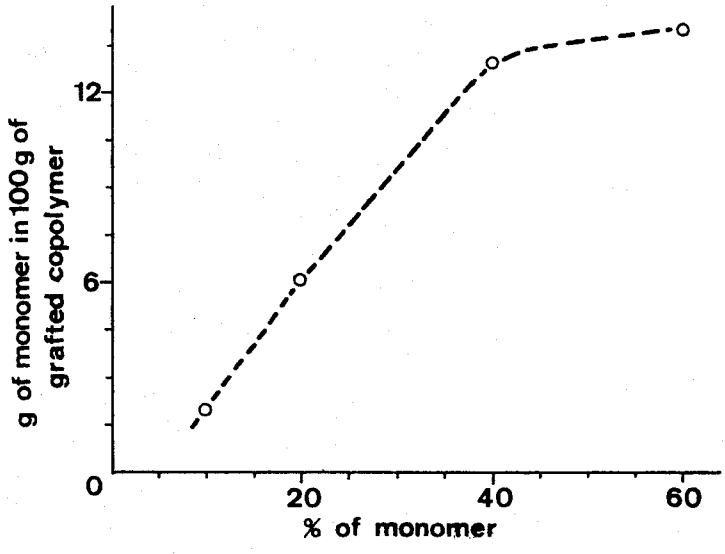

Fig. 1. Percentage of grafting *vs.* monomer concentration. T = 70 °C, time 20 hrs. Solution of polypropylene in benzene at 12 %. Bz_2O_2 2 %

From the experimental data and the value of k_p drawn from literature[16], we calculated, from Eqs. (13) and (14), the concentration [S•] in mole/l. of the backbone active centres. Its average value, in the first hours of the reaction is $\sim 2 \cdot 10^{-8}$ mole/l. The behaviour of Q/G is practically linear with time in the first hours of the reaction and subsequently it tends to an asymptotic value. The results obtained yield values for the

concentration of [S•] of the same order of magnitude as the concentrations found in the usual radical polymerizations in spite of the approximations involved in the simplified scheme.

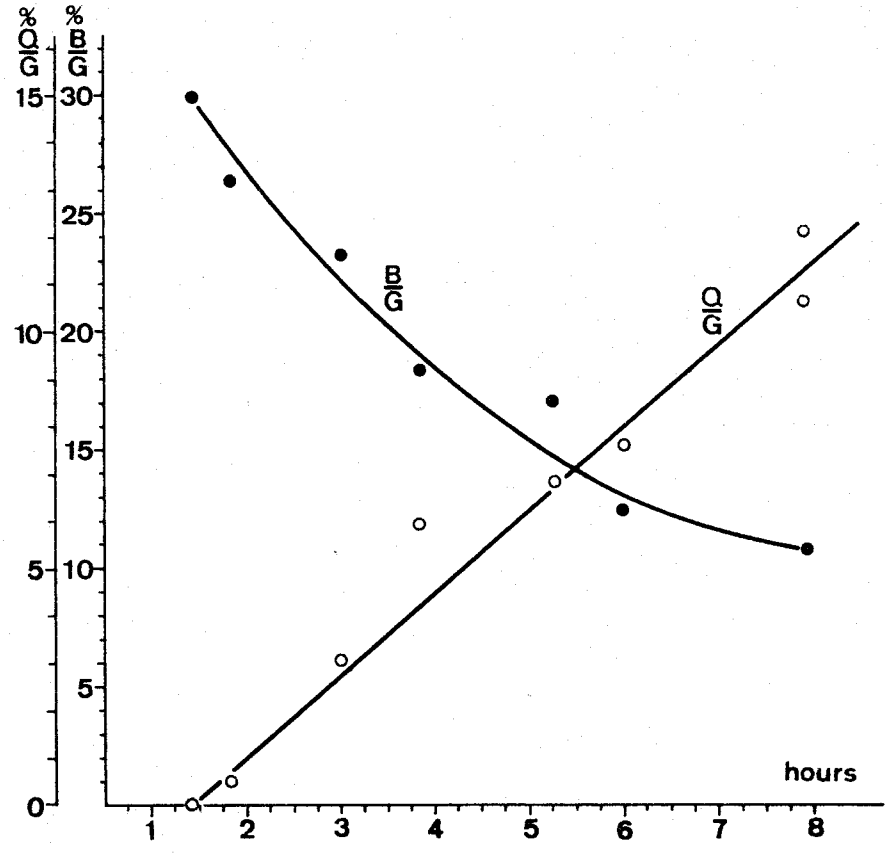

Fig. 2. Ratios of monomer to initial polypropylene B/G and of grafted monomer to initial polypropylene Q/G *vs.* time

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