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Free-Radical Modification of Polypropylene. I. Grafting of Poly(Ethyl Acrylate) on Atactic Polypropylene*

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ABSTRACT

The synthesis of atactic poly(propylene-g-ethyl acrylates) of $\overline{M}_n \sim 3000$-5000 has been accomplished with 80-90% incorporation of the backbone in the graft copolymer. The principle involves free radical initiation of ethyl acrylate polymerization with benzoyl peroxide via chain transfer. At low conversions (up to ~15%), massive homopolymerization took place and the initial rates of both homo- and graft copolymerizations were indistinguishable even with 1% initiator based on monomer. Grafting occurred at higher conversions and the $\overline{M}_n$ of the grafted product increased with increasing initiator concentration for almost similar conversion data. The isothermal stability of the graft copolymer was far superior to that of atactic polypropylene. The initial decomposition temperature of the graft copolymers increased with increasing initiator amount used for grafting. It is proposed that the number of branches of poly(ethyl acrylate)

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increased, following the abstraction of an increasing number of tertiary hydrogen atoms from the backbone.

INTRODUCTION

Chemical modification of polymeric materials to impart desirable properties by grafting is a widely practiced technique. Polypropylene, a popular material, has certain drawbacks, like photochemical and thermal instability, poor water absorption, and dyeability. Easy degradation of atactic polypropylene is attributed to the presence of tertiary hydrogens along the chain. A review article has recently been published on the chemical modification of polypropylene [1].

Atactic polypropylene is a by-product of the polypropylene industry, which uses Ziegler-Natta catalysts, and amounts to 3-10% of total polypropylene production. The molecular weight of atactic polypropylene varies considerably from grade to grade. The low molecular weight product does not have any profitable outlet.

The history of graft modification of polypropylene goes back to the late 1950s when Natta et al. [2] successfully used hydroperoxidic derivatives of crystalline and amorphous poly-α-olefins as initiators. In general, the tertiary hydrogen atoms in polypropylene offer two distinct possible modes for free-radical grafting: i) oxidation to hydroperoxide and subsequent decomposition to free radicals with or without a catalyst, and ii) chain-transfer initiation.

Chain-transfer initiation is partially responsible for branching in the polymer molecules, the extent of which increases with increasing polymer/monomer ratio and conversion. The site of attack may be located either in the substituent of the chain itself, e.g., a tertiary hydrogen atom or an α-allylic hydrogen atom [3-5]. Temperature as well as nature of the solvent, monomer, and initiator have pronounced effects on grafting [6]. Most of the published literature deals with relatively high molecular weight atactic polypropylenes. Low molecular weight graft copolymers are preferred in certain applications. Therefore, we undertook a study of the graft copolymerization of acrylates on low molecular weight atactic polypropylene ($\overline{M}_n$ 1500) using benzoyl peroxide as the free radical initiator. This paper deals with the graft copolymerization of ethyl acrylate in xylenes at 80 ± 2°C.

EXPERIMENTAL

Materials

Ethyl acrylate, EA (Indian Petrochemicals Corp., Ltd.; IPCL), was thoroughly washed by the standard procedure to remove inhibitor and dried. Xylenes (IPCL) with the following composition of GC analysis was used as received; saturates, 2.29%; benzene, 0.11%; toluene, 2.15%; ethylbenzene, 19.36%; p-xylene, 11.85%; m-xylene, 56.05%; and o-xylene, 8.18%. Atactic polypropylene, APP (IPCL), was dissolved in xylenes at room temperature and filtered. The filtrate was examined for solid content and used for the graft copolymerization. Benzoyl peroxide, BP (BDH), was used as received.

Polymerization

Polymerizations were carried out in a three-neck flask fitted with pressure-equalized dropping funnel, magnetic stirrer, thermometer pocket, and double-wall condenser with provision to maintain an N_2 blanket. Conditions were established to insure no solvent loss during polymerization at 80 ± 2°C, with the help of control runs. The required amount of EA was added to the APP solution through the pressure-equalized dropping funnel and equilibrated at 80 ± 2°C. A known volume of sample was withdrawn to determine and establish the initial solid content. A concentrated solution of BP was added to trigger the polymerization. For kinetic data, known aliquots were withdrawn from time to time, poured into a small amount of 1% methanolic solution of hydroquinone, and dried to constant weight. The monomer conversions were taken to ~60-90% for analysis of the polymer, solvent was removed under reduced pressure, and the polymer was dried to constant weight in a vacuum oven at 40°C.

Extraction

Crude polymer samples were extracted with boiling n-hexane for 8 h. The insoluble fraction, containing poly(ethyl acrylate), PEA, and the graft copolymer APP-g-PEA was dried and weighed. For IR analysis, the polymer was purified by repeated precipitation in petroleum ether (40-60°C) from benzene solution.

Analyses

$\overline{M}_n$'s were determined in a Hewlett-Packard 302 B vapor pressure osmometer in chloroform at 37°C. IR spectra were recorded with a Perkin-Elmer 567 spectrometer. Thermal analyses were carried out with a Du Pont 990 thermal analyzer coupled with 943 thermogravimetric analyzer.

RESULTS AND DISCUSSION

The rates of EA polymerization in the presence of APP ($\overline{M}_n$ 1500) in xylenes increased with increasing concentration of BP (0.08-1%

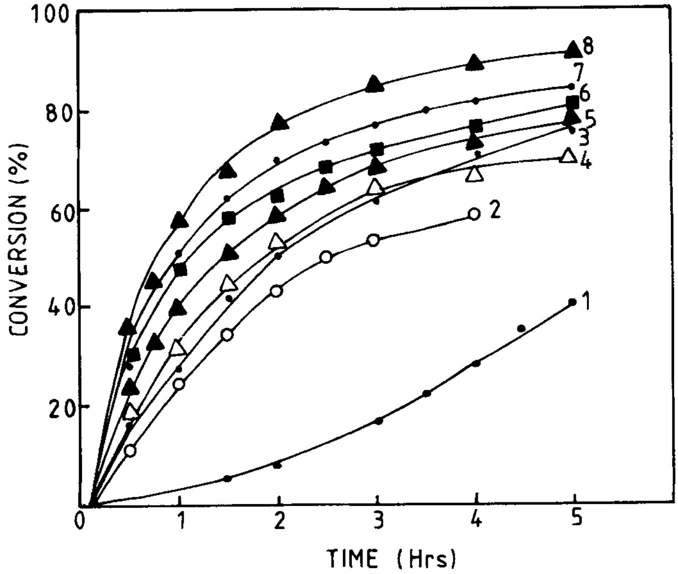

FIG. 1. Conversion-time plots for graft polymerization of EA on APP with varying BP concentration (based on EA) at 80 ± 2°C. APP, 8 g; EA, 36 g; xylenes, 200 mL. BP: 0.08% (1), 0.1% (2), 0.2% (3), 0.4% (4), 0.6% (5), 0.8% (6), 1% (7, with 8.42 g APP), and 1% (8, without APP).

based on EA), as is routinely experienced in free-radical polymerizations. Except for 0.08 and 0.1% BP, which gave ~60%conversion in 10 h, 60-80% conversions were generally obtained in 5 h at 80 ± 2°C (Fig. 1). An induction period of 8-10 min was observed in all cases. Separate sets of polymerizations were carried out up to 15% conversions, and initial rates of reactions R_0's were calculated. Both graft copolymerization and homopolymerization of EA resulted in similar R_0 values for similar concentrations of EA. The second-order dependence on EA at relatively high monomer concentrations (0.369-1.475 M) indicates primary radical termination (Figure 2). Similar R_0 values were obtained on varying the APP concentration (Table 1). For a change in [EA]/[t-H] from 2.59 to 1.76 with 6.10 × 10^{-2} M BP, the initial rates were constant within experimental error (Nos. 19 to 22). These results strongly suggest that grafting did not occur at such low conversions (15%). Had there been grafting, the rates of homo- and graft copolymerizations would have been different.

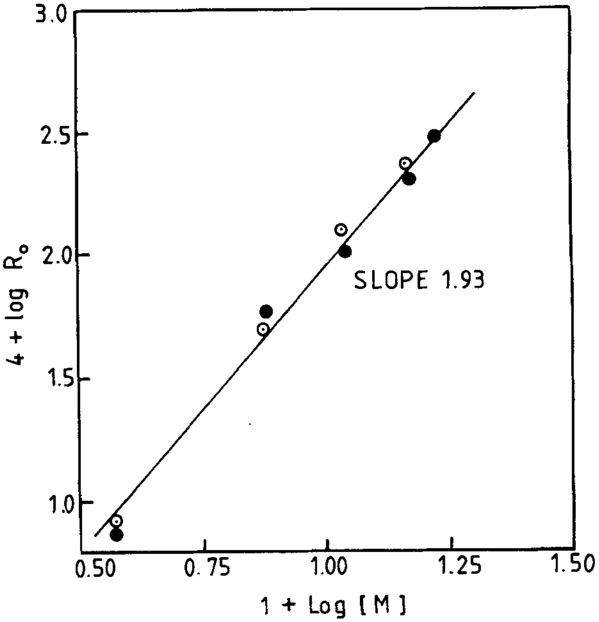

FIG. 2. Plots of log R_0 vs log [M] for polymerizations of EA in the absence (●) and the presence of 7.9 g APP (○) in xylenes at 80 ± 2°C; BP 0.8%.

Grafting by the radical chain-transfer process involves the following fundamental steps:

$$R\text{–}R \xrightarrow{k_d} 2R^{\cdot} \tag{1}$$

$$R^{\cdot} + M \xrightarrow{k_i} RM^{\cdot} \tag{2}$$

$$RM^{\cdot} + nM \xrightarrow{k_p} P_1^{\cdot} \tag{3}$$

$$R^{\cdot} + P_2 \xrightarrow{k_a} P_2^{\cdot} + RH \tag{4}$$

$$P_1^{\cdot} + P_2 \xrightarrow{k_a'} P_2^{\cdot} + P_1H \tag{5}$$

TABLE 1. Polymerization of EA in the Presence of APP in Xylenes at 80 ± 2°C; Total Volume, 244 mL; Conversions up to 15%

No.	APP, g	[t-H],[a] M	[EA], M	[BP], M × 10^3	R_0, M/L·min × 10^2
15	0	-	0.369	1.52	0.07
16	7.9	0.777	0.369	1.52	0.08
17	0	-	1.106	4.57	1.21
18	5.9	0.580	1.106	4.57	1.26
19	5.8	0.570	1.475	6.10	2.15
20	7.9	0.777	1.475	6.10	2.50
21	7.9	0.777	1.475	6.10	2.46
22	8.5	0.836	1.475	6.10	2.32

[a] Concentration of tertiary hydrogen of APP backbone.

$$P_2^\cdot + M \xrightarrow{k_i'} P_2M^\cdot \tag{6}$$

$$P_2M^\cdot + nM \xrightarrow{k_p'} P_2P_1^\cdot \tag{7}$$

$$P_1^\cdot + P_2^\cdot \xrightarrow{k_t} P_1P_2 \tag{8}$$

where M, P_1, and P_2 are monomer, polymer chain from M, and polymer backbone, respectively. Grafting on P_2 results according to Reactions (4) and (5). Energetically, Reaction (2) is favored over Reactions (4) and (5). Also, the addition of monomer to the macroradicals is dependent on the reactivity and polarity of both radical and monomer [7]. In other words, if grafting takes place, k_i'/k_i and k_i'/k_p should not be insignificant. The failure to detect graft copolymers suggests that Reactions (4) to (8) are insignificant at low conversions. At relatively higher conversions, however, appreciable grafting took place (Table 2), and the extent was examined as a function of initiator concentration. This is in line with the results plotted in Fig. 1. Curves 7 and 8 represent the polymerization of EA in the presence and absence of APP, respectively, under identical experimental conditions. The former has a lower rate beyond ~15% conversion.

The Arrhenius parameters for hydrogen abstraction from R_3CH by $PhCOO^\cdot/Ph^\cdot$ in solution are not known. The activation energies of

TABLE 2. Grafting of PEA on APP in Xylenes at 80 ± 2°C with Varying Amounts of BP (based on EA) and Extraction Data. APP, 10 g; EA, 36 g; 244 mL, 5 h

			Results after extraction with boiling n-hexane			
No.	BP, %	Conversion, %	Unreacted APP, g	Grafted APP, g	APP grafted,[b] %	$\overline{M}_n$
9[a]	0.08	58	0.96	9.04	90.40	3300
10[a]	0.10	60	1.20	8.80	88.00	3100
11	0.20	70	1.70	8.30	83.00	3500
12	0.40	65	1.80	8.20	82.00	3000
13	0.60	75	1.90	8.10	81.00	3700
14	0.80	73	2.00	8.00	80.00	5000
14a[c]	0.80	75	-	-	-	4000

[a] Polymerization for 10 h.
[b] Of total APP used.
[c] Control run without APP.

propagation and abstraction of tertiary hydrogen by Ph· in the gas phase are of the same order, i.e., 6-8 kcal/mol [8, 9]. Assuming the reactivity of PEA· to be equal to Ph· or PhCOO· for the abstraction of tertiary hydrogen from isobutane and using transfer constants for CCl_4 for reactions, one obtains for

$$Ph^{\cdot} + CCl_4 \longrightarrow PhCl + CCl_3^{\cdot}$$

and

$$PEA^{\cdot} + CCl_4 \longrightarrow PEACl + CCl_3^{\cdot}$$

$k_p/k_a' \approx 5400$ [10-12]. This is an oversimplification, because the reactivities of PEA· and Ph· are different. Nevertheless, this gives an idea of the relative frequencies of Reactions (3) and (5). Probably, both abstraction Reactions (4) and (5) are operative in graft copolymerization. Tertiary hydrogen abstraction from APP at 80 ± 2°C may be appreciable when part of the EA is consumed. It has been pointed

TABLE 3. Thermogravimetric Analyses of the Mixture of APP-g-PEA and PEA Obtained with Varying Amounts of BP

No.	BP,[a] %	Temperature of initial decomposition, °C	Temperature of 90% weight loss, °C
9	0.080	180	430
10	0.100	200	470
11	0.200	220	460
12	0.400	230	430
13	0.600	260	450
PEA	0.800	265	440

[a] Based on EA.

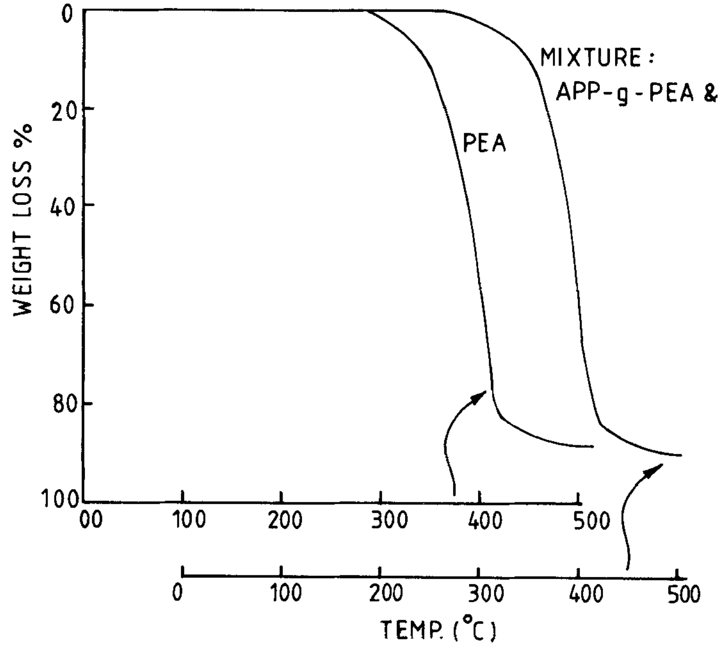

FIG. 3. Thermogravimetric analyses of pure PEA and (APP-g-PEA plus PEA) obtained in the absence and the presence of APP with 0.8% BP at 80 ± 2°C; heating rate, 10°C/min; N_2, 110 mL/min.

out by Natta et al. [13] that, in the methyl acrylate-APP system at 70°C, the average value of active centers on APP in the first hours of polymerization is of the same order of magnitude as that usually found in free-radical polymerization.

The absence of crosslinked polymer and higher incorporation of APP in the present graft copolymer (78-90%) corroborate the above views. An attempt to separate PEA from APP-g-PEA by extracting with methanol and methanol/water (75/25) failed, because of the low $\overline{M}_n$ of the mixture (3100-5000). Both soluble and insoluble portions showed absorptions at 5.75 and 7.3 μm characteristic of acrylate and polypropylene, respectively. For similar conversions in Nos. 11, 13, and 14, there is a gradual increase in $\overline{M}_n$ with increasing BP concentration (Table 2). The control run, i.e., polymerization of EA in the absence of APP with 0.8% BP, yielded PEA of $\overline{M}_n \approx 4000$. This indicates that tertiary hydrogens have been abstracted from APP. Although estimation of the actual number of grafting sites was not possible because separation could not be achieved this is in agreement with the thermal stability of the PEA and APP-g-PEA blends. While APP decomposed within a few minutes, all the graft samples were stable at 120°C in air (flow of 110 mL/min, checked up to 3 h). Moreover, thermogravimetric analyses of pure PEA and the blends are comparable (Table 3 and Fig. 3). The initial decomposition temperature of the graft copolymers is strongly dependent on the concentration of BP used; it increased with increasing initiator level, in full agreement with the view proposed. Further studies are in progress and will be communicated later.

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