Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Samoilov, S. M.(1983) 'Propylene Radical Copolymerization with Vinyl Acetate, Methyl Acrylate, Dimethyl Maleate, and Diethyl Fumarate', Journal of Macromolecular Science, Part A, 19: 1, 107 — 122
To link to this Article: DOI: 10.1080/00222338308069426
URL: http://dx.doi.org/10.1080/00222338308069426

J. MACROMOL. SCI.–CHEM., A19(1), pp. 107-122 (1983)

Propylene Radical Copolymerization with Vinyl Acetate, Methyl Acrylate, Dimethyl Maleate, and Diethyl Fumarate

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ABSTRACT

Propylene (Pr) radical copolymerization (in water emulsion) with vinyl acetate (VAc), methyl acrylate (MA), dimethyl maleate (DMM), and diethyl fumarate (DEF) has been studied and is discussed, together with literature data on other Pr radical copolymerization reactions. Composition diagrams of the systems studied are presented. Pr relative activity is determined primarily by polarity and to a lesser degree by resonance stabilization of the comonomers as described by the "Q-e" scheme. Pr reacts actively and gives alternating copolymers when comonomer has relatively high electronegativity ($e > 1.2$) and low resonance stabilization (e.g., DMM, tetrafluoroethylene, maleic anhydride). A decrease of comonomer electronegativity (e.g., VAc, vinyl chloride) and/or an increase of resonance stabilization (e.g., MA, DEF, acrylonitrile) result in a noticeable decrease of Pr activity and in a lower Pr concentration in the copolymers as compared to the comonomer mixture. The mechanism of these effects is discussed. Properties of Pr copolymers with VAc, MA, DMM, and DEF (also with butyl acrylate and vinyl alcohol) are described. Molecular weight decreases rapidly with an increase of Pr

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0022-233X/83/1901-0107$3.50/0

content in each type of copolymer. Copolymers with different comonomers, compared in the series Pr-MA, Pr-VAc, Pr-DEF, Pr-DMM, are characterized (in general) by an increase of Pr content and by a decrease of molecular weight (from ~150,000 to ~8,000). In Pr-VAc and Pr-MA copolymers, glass transitions shift to lower temperatures (approximately according to the Gordon equation) with an increase of Pr content. No transitions were found in Pr-DMM and Pr-DEF copolymers (in the range -100 to +100° C). Thermostability of the copolymers (in air and nitrogen) does not depend on Pr content and/or molecular weight and becomes higher in the series Pr-VAc $<$ Pr-MA $\simeq$ Pr-DEF $<$ Pr-DMM.

Propylene (Pr) copolymerization with functional monomers is an interesting problem from both academic and practical points of view. The well-known facts that ethylene copolymerization with polar comonomers via ionic mechanism has as yet been unsuccessful as compared to the very fruitful radical route for such reactions of ethylene indicate that a radical mechanism might likewise be potential for the synthesis of Pr copolymers with polar functional comonomers. Indeed, although Pr is commonly considered as a monomer which is not suitable for radical polymerization reactions, it was recently demonstrated that Pr can effectively copolymerize via a "classic" radical mechanism with several functional comonomers [1]. (Pr reactivity in radical copolymerization can be substantially enhanced by the so-called "charge transfer agents" [2], but this subject is not considered in the present study.)

The kinetics of Pr copolymerization reactions tend to depend on comonomer polarity expressed by the "e" factor in the "Q-e" copolymerization scheme. Comonomers with a comparatively high (>1.2) "e" factor (high electrophilic comonomers, e.g., tetrafluoroethylene, maleic anhydride) copolymerize with Pr in alternating reactions that give products with molecular weights up to ~200,000. On the other hand, Pr copolymers with lower polarity monomers (e.g., with vinyl chloride or vinyl acetate, "e" 0.20 and -0.22, respectively) have a noticeably lower Pr content compared to the comonomer mixture, and with an increase of Pr content in the copolymers their molecular weight decreases rapidly.

Difficulties in Pr radical polymerization can be plausibly explained by assuming that Pr easily gives up $H^{\cdot}$ atoms (an explanation of Pr high chain transfer activity and of low molecular weight of Pr homo- and most copolymers), forming resonance stabilized allyl radicals $CH_2 \cdots CH \cdots CH_2$ which are inactive in joining the growing polymer chains (an explanation of Pr inactivity in propagation reactions and of low Pr content in most copolymers). Also, to interpret a much higher Pr activity in reactions with high electrophilic comonomers, we can assume that such comonomers can form with nucleophilic Pr biradical donor-acceptor complexes of the type: $CH_3{-}CH^{\bullet}{-}CH_2^{\oplus} \cdots {}^{\ominus}CR_1R_2{-}C^{\bullet}R_3R_4$, that these complexes can homopolymerize further into alternating copolymers, and that displacement of Pr π-electrons in the presence of electrophilic comonomers impedes the formation of stabilized allyl radicals.

Still, the data on Pr radical copolymerization are too limited to generalize the mentioned classification of the comonomers. For example, Pr radical copolymerization with acrylonitrile, which can be described as a high electrophilic monomer ("e" 1.20), does not proceed as an alternating reaction, and Pr-acrylonitrile copolymers contain substantially less Pr than the comonomer mixture over the entire range of the monomer composition [1, 3, 4]. Information on the properties of Pr copolymers is also very scarce.

The prime objective of this paper is to compare the reactivities of monomers in Pr radical copolymerization with low polarity comonomers [vinyl acetate (VAc) and methyl acrylate (MA)] and with high electrophilicity comonomers [dimethyl maleate (DMM) and diethyl fumarate (DEF; the polarity of the comonomers is specified according to the value of "e" factor, Table 1)]. It is also of interest to describe some properties of these copolymers. Among the comonomers studied in the present research, only VAc has been copolymerized before with Pr [1]. Radical copolymerization of Pr with MA, DMM, DEF, and butyl acrylate (the latter has also been investigated) are new reactions. All reactions were carried out in water emulsion.

EXPERIMENTAL

Reactions were carried out in a 1-L stainless steel stirred (600-1000 rpm) autoclave, placed on a scale to directly measure (accuracy ± 15 g) the amount of Pr in the reaction mixture. Emulsions were prepared in distilled water (30-45%) solutions of nonionic emulsifiers (1-3% polyoxyethylene nonylphenols) without or in combination with an anionic emulsifier (~0.25% dodecylbenzene sodium sulfonate). Emulsions contained stabilizer (~0.8% hydroxyethylcellulose), buffer (~0.2% $NaHCO_3$), and initiator [~0.2% $Na_2S_2O_8$ or $(NH_4)_2S_2O_8$ without or in combination with ~0.3% $NaHSO_3$ or with ~0.01% tert-butyl hydroperoxide and ~0.05% cyclohexanone peroxide; the concentration of all components is given in weight % in relation to the total reaction mixture, including Pr and comonomer].

The autoclave, charged with emulsified comonomer, was purged with Pr and heated to the reaction temperature that was kept at a constant level in the 40-80°C range. Liquid Pr was pumped into the reactor at room temperature and/or after attaining the reaction temperature. Additional amounts of Pr were introduced during the reaction to keep the pressure at a constant level in the 15-120 atm range. Pr concentration in the comonomer mixture is calculated in

TABLE 1. "Q-e" Factors [5] of the Comonomers used in Radical Copolymerization with Propylene and Propylene Copolymerization Activity

		"Q-e" factors			
Comonomer	Designation	Q	e	Pr reactivity	Refs.
Propylene	Pr	0.002	-0.78	-	-
Vinyl acetate	VAc	0.026	-0.22	Lower than VAc	1, 6-8
Ethylene	Et	0.015	-0.20	Lower than Et	1
Vinyl chloride	VCl	0.044	0.20	Lower than VCl; statistical distribution of Pr units in copolymers	1, 9, 10
Methyl acrylate	MA	0.420	0.60	Much lower than MA	This paper
Butyl acrylate	BA	0.500	1.06	-	This paper
Acrylonitrile	AN	0.600	1.20	Lower than AN	1, 3, 4

Tetrafluoroethylene	TFE	0.049	1.22	Similar to TFE; alternating copolymers with the presence of adjacent Pr units	1, 11-13
Diethyl fumarate	DEF	0.610	1.25	Somewhat lower than DEF	This paper
Dimethyl maleate	DMM	0.090	1.27	Similar to DMM; alternating copolymers	This paper
Chlorotrifluoroethylene	CTFE	0.020	1.48	Similar to CTFE; alternating copolymers	14, 15
Trifluoroacrylonitrile	FAN	0.040	1.92	Similar to FAN; alternating copolymers	1, 16
Maleic anhydride	MAn	0.230	2.25	Similar to MAn; alternating copolymers	1, 17
Methyl trifluoroacrylate	MFA	0.035	2.37	Similar to MFA; alternating copolymers	1, 18
Sulfur dioxide	SO_2	-	-	Similar to SO_2	1, 19

relation to the total amount of Pr introduced into the reactor. The reaction time was 20-22 h. The phase composition of the reaction mixture is not known, but we can suppose that at the reaction conditions there was only a limited dissolution of Pr [20, 21] and all comonomers (very low solubility at atmospheric pressure) in water, and also that, besides possibly DMM, the comonomers were miscible with Pr (analogy with the miscibility of comonomers and light hydrocarbons). In this way we can suppose that during the reaction, Pr and most of the comonomers were probably in the form of a homogeneous mixture both in monomer droplets and in emulsion particles.

Conversion of the comonomers (calculated from copolymer composition and from residual comonomer content in the product) was in the 30-100% range. There was no clear correlation between Pr concentration in the monomer mixture and the reaction rate. The products were emulsions that contained 15-50 wt% polymers (after correction for the initial solid components) with ~80% particles having ~0.25 μm and the rest ~0.90 μm diameter (Joyce-Loebl method).

In a special series of experiments the reaction pressure was raised and kept constant by introducing N_2 into the reactor, first charged with Pr-VAc initial emulsion (Table 2). In these experiments the Pr content in the copolymers increased both with an increase of Pr content in the monomer mixture at constant pressure (Experiments A-C) and with a decrease of N_2 pressure at constant comonomer composition (Experiments C-F). The latter effect is probably related to a change in comonomer composition in the emulsion droplets and micelles as a result of variation in N_2 pressure. The increase of N_2 pressure brought about a noticeable increase in polymer yield (solids in emulsion) and molecular weight (Experiments C-F). The copolymer glass transition temperature was primarily dependent on the Pr content (Experiments A-C) and to a much lesser degree on the molecular weight (Experiments C-F).

Copolymers were separated by coagulation of the emulsions at ~0°C, purified by dialysis in distilled water, and dried in vacuum to constant weight at 40°C. Some Pr-VAc and Pr-MA copolymers were additionally purified by reprecipitation (at room temperature from acetic acid into water; Pr-DMM and Pr-DEF do not dissolve in acetic acid) and drying in vacuum. Pr-VAc copolymers that had been boiled with a molar excess of aqueous alkali were completely hydrolyzed, but had the same molar concentration of Pr as the unhydrolyzed copolymers. Comonomer concentration in the copolymers was determined by proton-NMR analysis (in DMSO solutions, see Fig. 1) and verified by carbon elemental analysis. The relative concentration of the comonomers in dry films, cast directly from the emulsions, was determined (NMR) with regard to other components of the emulsions and coincided with the composition of the samples purified by precipitation.

Pr-VAc copolymers are tough white resins that become softer and

TABLE 2. Effect of N_2 Pressure on Propylene-Vinyl Acetate Emulsion Copolymerization (in equal, besides indicated, reaction conditions)

	Reaction		Propylene			Copolymer	
Experiment	Pressure (atm)	Temperature (°C)	In monomer mixture (mol%)	In copolymer (mol%)	Solids in emulsion (wt%)	Solution viscosity ($[\eta]/[\eta]_A$)	T_g (°C)
A	110	37	63	24.5	8.1	1.00	13
B	110	42	55	17.0	9.2	-	15
C	110	42	36	9.5	23.4	0.90	25
D	77	40	36	11.2	15.6	0.90	24
E	38	40	36	14.2	7.6	0.33	20
F	8	38	36	13.2	8.2	0.09	23

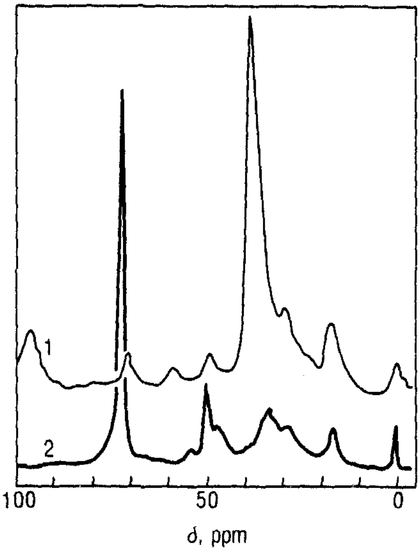


FIG. 1. NMR spectra of (1) propylene-vinyl acetate (11.0 mol% Pr) and (2) propylene-methyl acrylate (15.6 mol% Pr) copolymers.

yellow with an increase of Pr content; Pr-MA are colorless, flexible, and slightly sticky; Pr-butyl acrylate (Pr content 10-12 mol%) are colorless, transparent, tough, sticky elastomers; Pr-DMM are either white and hard or soft and slightly sticky; Pr-DEF are grey, flexible, and sticky; and Pr-vinyl alcohol copolymers are brittle light-yellow resins. The later copolymers, depending on their composition, are soluble (~ 10 mol% Pr) or insoluble (~ 20 mol% Pr) in hot water. Copolymers with VAc, MA, DMM, and DEF are amorphous (x-ray). All copolymers studied formed flexible transparent films.

The molecular weight of Pr-VAc and Pr-MA copolymers was evaluated by viscometry (80% acetic acid-20% water solutions at 25°C) and by GPC (hexafluoroisopropanol solutions) using poly-VAc and poly-MA fractions of known molecular weight for comparison. In addition, the viscometric data were tested by the equation

$$[\eta]\ \mathrm{dL/g} = 6.96 \times 10^{-5} \times M^{0.78}$$

useful for the calculation of poly-VAc molecular weight [22]. The molecular weights of Pr-DMM and Pr-DEF copolymers were evaluated by GPC (in DMSO, relative to polystyrene standards). DSC was performed with a DuPont 900 instrument in N_2 atmosphere at a heating rate of 10°C/min with samples purified by reprecipitation and free from surfactants (dialysis in water was not efficient enough to have

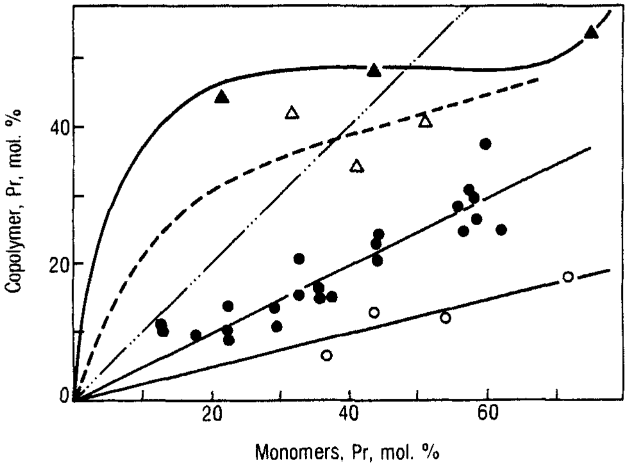


FIG. 2. Composition diagrams (monomer mixture-copolymer) for Pr radical (emulsion) copolymerization with vinyl acetate (●), methyl acrylate (○), dimethyl maleate (▲), and diethyl fumarate (△). The azeotrope line is shown as – ···.

the DSC curves free from transitions of the residual surfactants). Glass transitions of the copolymers were identified by the onset (intersection of tangent lines) of stepwise deviations on DSC curves. TGA was performed with a DuPont 990 instrument in N_2 and air atmosphere at a heating rate of 15° C/min.

DISCUSSION

Comonomer Reactivity

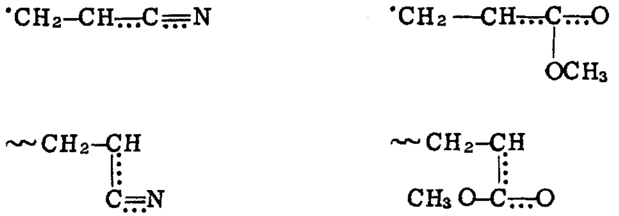
Composition diagrams (monomers-copolymer) for the systems studied are shown in Fig. 2. (The present Pr-VAc composition diagram (Fig. 2) is very close to the diagram that has been calculated from the literature data [1].) It is clear that in a wide range of monomer composition (up to ~75 mol% Pr content) Pr is noticeably less reactive compared to VAc and especially compared to MA (Pr concentration in the copolymers did not exceed ~35 mol% for Pr-VAc and ~18 mol% for Pr-MA copolymers). It is also certain that Pr-DMM copolymers have approximately equimolar composition (48-57 mol% Pr in the copolymers) and that Pr copolymerization with DMM proceeds mostly as an alternating reaction.

The data for Pr-DEF are less conclusive as in this case the monomer composition range (34-53 mol% Pr) was comparatively narrow and the copolymer composition (38-44 mol% Pr) can correspond to different combinations of comonomer reactivity ratios. Nevertheless, it is certain that in copolymerization with DEF the reactivity of Pr is substantially higher than in reactions with VAc and MA and also that Pr is probably somewhat less reactive with DEF than with DMM. We assume for the Pr-DEF system a composition diagram (dashed line in Fig. 2) which is closer to the Pr-DMM alternating one than to the low Pr activity diagrams of Pr-VAc and Pr-MA reactions. Although the data shown in Fig. 2 relate to high conversion of comonomers (see above), the general character of the described correlations should probably also take place at lower conversions because in all our systems the change of Pr concentration in the monomer mixture during the reaction was in the same direction: to higher Pr concentration.

Pr reactivity in different radical copolymerization reactions, explored in this study and known from the literature, is summarized in Table 1 together with "Q-e" values for the comonomers. We can see that our data support in general the approach suggested above: to correlate Pr reactivity primarily with polarity of comonomers. When the polarity factor "e" is below a certain limit (on the basis of our data for the Pr-MA system we can now better define this limit as ~0.6), Pr is noticeably less active compared to the comonomer, Pr copolymers contain less Pr than the monomer mixture and Pr units are evidently statistically distributed in macromolecules (the latter fact was experimentally proved for Pr-VCl copolymers). On the other hand, Pr copolymerization with most electronegative comonomers, characterized by a higher "e" factor (> 1.2), is in general an alternating reaction although, as was demonstrated for Pr-TFE, there is also a notable probability to have adjoining Pr units in the copolymers.

At the same time, we have four monomers (AN, TFE, DEF, DMM) with approximately the same "e" value (1.20-1.27) and only two (TFE, DMM) react with Pr in an alternating reaction as suggested above. Our data on lower Pr relative activity in copolymerization with DEF are of the same type as those reported for the Pr-AN system. These facts confirm each other and need additional explanation. We can see that among the studied comonomers both DEF and AN have a substantially higher resonance factor "Q" (Q_{AN} 0.60, Q_{DEF} 0.61 compared, for example, to Q_{TFE} 0.05, Q_{DMM} 0.09). We can also notice the comparatively high "Q" factor (0.42) for MA and compare this fact with the lower Pr reactivity in copolymerization with MA than with VAc (Q_{VAc} 0.026) and VCl (Q_{VCl} 0.044). (Pr reactivity in copolymerization with VCl is close to that with VAc [1].) Evidently resonance factor "Q" of the comonomers has a noticeable effect on Pr reactivity, and an increase of the comonomer "Q" value results in lower Pr relative activity which is opposite to the effect of a comonomer "e" increase.

To rationalize the correlation between resonance stabilization and relative activity of the comonomers, we suggest the following mechanism. The resonance takes place between the free valency and the polar substituent both in monomeric radicals and in macroradicals. On the one hand, this effect stabilizes the free valency of the monomeric radical and, on the other hand, it destabilizes the free valency of the macroradical as illustrated by



$^{\bullet}CH_2{-}CH\cdots C\equiv N$ $\quad$ $^{\bullet}CH_2{-}CH\cdots C(OCH_3)\cdots O$

$\sim\!\sim CH_2{-}CH(\cdots C\equiv N)$ $\quad$ $\sim\!\sim CH_2{-}CH(\cdots C(OCH_3)\cdots O)$

[Resonance stabilization factor "Q" relates to the radical formed after opening of the double bond, and should not be confused with resonance stabilization of the radical formed after separation of the $H^{\bullet}$ atom. For example, a high resonance stabilization and, as a result, a low activity of the allyl radical (see above) is a different effect from a very low resonance stabilization of the Pr radical $^{\bullet}CH_2{-}^{\bullet}CH{-}CH_3$, which is another cause of the low Pr activity in radical polymerization.] As a result, the activity of comonomeric radicals becomes higher but the activity of macroradicals with comonomer end units becomes lower. These effects end in higher relative copolymerization activity of comonomer as compared to Pr.

Copolymer Molecular Weight

Both solution viscosity and GPC show that for the same Pr-comonomer system the molecular weight of all studied copolymers decreases rapidly with an increase of Pr content in the monomer mixture and respectively in the copolymers (Fig. 3). There is no difference, in this aspect, between high (DMM, DEF) and low (VAc, MA) polar comonomers. A similar effect of molecular weight decrease with an increase of Pr content also takes place in Pr radical copolymerization with other high (e.g., TFE) and low (ethylene, vinyl chloride) polar comonomers [1]. (Pr-maleic anhydride copolymerization is an interesting exception with a maximum molecular weight at ~ 70 mol% Pr in the monomer mixture [1, 23].)

A decrease of copolymer molecular weight with an increase of Pr content can in general also be noticed when copolymers with different second comonomers are compared (Fig. 3). Thus, in general, molecular weight and Pr content of different copolymers explored in this study follow directly opposite orders:

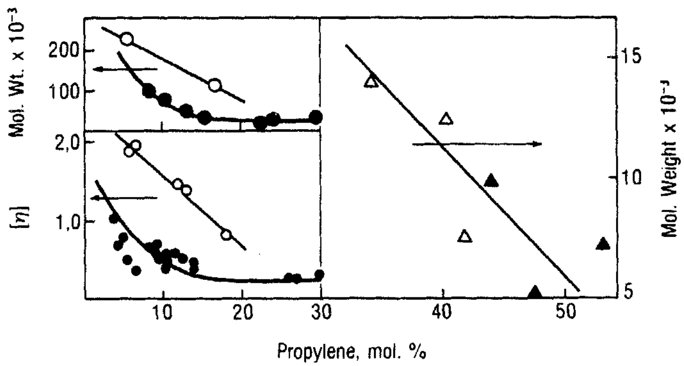


FIG. 3. Molecular weights ([η], viscosity of solutions) of Pr-VAc (●), Pr-MA (○), Pr-DMM (▲), and Pr-DEF (△) copolymers as functions of Pr concentration in the copolymers.

Pr content (Pr-DMM) > (Pr-DEF) > (Pr-VAc) > (Pr-MA)

Molecular weight (Pr-MA) > (Pr-VAc) > (Pr-DEF) > (Pr-DMM)

Note that the molecular weight of Pr-MA copolymers (above ~ 100,000) was noticeably higher than that of Pr-VAc copolymers (below ~100,000), and that in comparison with Pr-VAc and Pr-MA, the molecular weights of Pr-DEF (below ~15,000) and Pr-DMM copolymers (below ~10,000) were substantially lower (Fig. 3).

All these facts are evidently due to Pr high activity in chain transfer reactions together with low activity of Pr macroradicals in chain propagation. At the same time, there was no remarkable chain transfer to the CH_3-groups in acetate side units of Pr-VAc copolymers and no branching of the copolymers by this mechanism as no significant decrease of Pr-VAc molecular weight after hydrolysis of these copolymers was noticed.

Copolymer Glass Transitions

In the temperature range -100 to +100°C, glass transitions were determined for Pr copolymers with VAc, MA, and butyl acrylate. With an increase of Pr concentration the glass transitions of Pr-VAc and Pr-MA copolymers shift from the transition temperature of poly-VAc (~28°C [5]) and poly-MA (~10°C [5]) in the direction of the poly-Pr glass transition which is at a lower temperature (~-20°C [5], Fig. 4). The dependence of T_g on Pr content approximately follows the well-known Gordon equation:

$$\frac{1}{T_g} = \frac{X_A}{T_g^A} + \frac{X_B}{T_g^B}$$

(where T_g, T_g^A, and T_g^B are the glass transition temperatures of the copolymer and homopolymers; X_A and X_B are the comonomer concentrations in weight parts), and this is an argument that the T_g decrease in Pr-VAc and Pr-MA copolymers is mainly due to the presence of Pr units.

We can also notice that most deviations of experimental data from the Gordon equation are in the direction of lower T_g values than predicted by the equation. These deviations are evidently due to low molecular weight, and this was particularly characteristic for many of the analyzed Pr-VAc copolymers (see above). Thus the increase of Pr content in Pr-VAc and Pr-MA copolymers results in a decrease of the glass transition temperature primarily because of Pr incorporation into macromolecules and additionally due to a decrease of copolymer molecular weight.

The glass transition temperature of Pr-butyl acrylate copolymers (10-12 mol% Pr) was ~ -45°C and thus was displaced from polybutyl acrylate (-54°C [5]) in the direction of poly-Pr T_g. Pr-DMM and Pr-DEF did not show any noteworthy glass transitions in the temperature range -100 to +100°C.

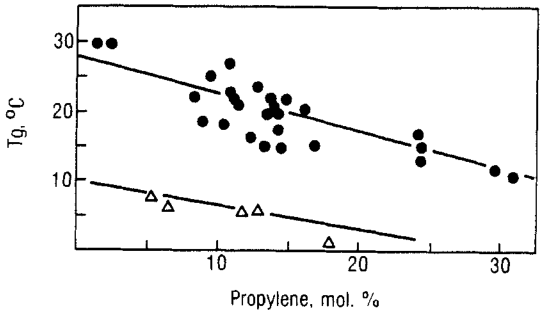


FIG. 4. Glass transition temperature (T_g) of Pr-VAc (●) and Pr-MA (△) copolymers as functions of Pr concentration in the copolymers. The lines show the relation between T_g and copolymer composition as defined by the Gordon equation.

TABLE 3. Thermostability of Propylene Copolymers

Polymer	Propylene in copolymer (mol%)	Temperature of TGA maximum weight loss rate (°C)	
		In air	In N_2
Pr-VAc	6.7	350	365
Pr-VAc	10.5	355	370
Pr-VAc	26.1	360	365
Pr-VAc	29.7	355	370
Pr-MA	6.0	400	-
Pr-MA	18.0	400	-
Pr-DEF	34.3	400	410
Pr-DEF	40.1	390	-
Pr-DMM	44.1	430	450
Pr-DMM	57.4	420	440
Poly-VAc (5×10^4 MW)	0	350	365
Poly-MA (10^5 MW)	0	400	-

Copolymer Thermostability

In air and in nitrogen, all the copolymers studied are thermostable up to ~200°C, start to rapidly decompose above 300-350°C, and show maximum rate of decomposition at 350-450°C (TGA data, the thermostability of the copolymers was slightly higher in nitrogen compared to air). In general, the differences in copolymer thermostability are primarily determined by the type of the second comonomer and depend much less on the molar composition and molecular weight of the copolymers (Table 3). The highest thermostability was found for Pr-DMM although they had a much lower molecular weight as compared to Pr-VAc and Pr-MA copolymers (see above). Pr-VAc showed the lowest thermostability with decomposition temperatures being ~ 70°C below those of Pr-DMM copolymers (in air and N_2, respectively). Pr-MA and Pr-DEF had intermediate and similar thermostability although the molecular weight of Pr-MA was much higher than that of Pr-DEF copolymers. The thermostability of Pr-VAc (0-30 mol% Pr) and Pr-MA copolymers (0-18 mol% Pr) was not affected by a change in Pr concentration or by an accompanying change of copolymer molecular weight. The thermostability of these copolymers was practically the same as the thermostability of poly-VAc and poly-MA.

SUMMARY

Pr relative activity in all known radical copolymerization reactions (including literature data) can be described as the activity which is to a high degree defined primarily by polarity and additionally by resonance stabilization of comonomers, expressed by the "Q-e" scheme. With low polarity comonomers (characterized by "e" $\leqslant$ 0.6, e.g., with VAc, MA), Pr relative activity is low and the copolymers contain substantially less Pr than the comonomer mixture. On the other hand, with higher polarity comonomers (e.g., with DMM, DEF), Pr reacts more actively and can give alternating copolymers (e.g., Pr-DMM). Pr activity is comparatively lower when resonance stabilization of comonomers is high (e.g., DEF, MA).

An increase of Pr concentration in copolymers with VAc, MA, DMM, and DEF is accompanied by a noticeable decrease in copolymer molecular weight. The same regularity can be seen by comparing, in general, copolymers of the different comonomers studied. In the comonomer series MA, VAc, DEF, DMM, the copolymerization activity of Pr (Pr concentration in comonomers) goes regularly up and copolymer molecular weight goes regularly down.

As a result of Pr incorporation into Pr-VAc and Pr-MA copolymers, with an increase of Pr concentration the glass transitions take place at lower temperatures and the T_g dependence on Pr content approximately follows the Gordon equation. There are no glass transitions seen in Pr-DMM and Pr-DEF copolymers (in the -100 to +100°C range).

The copolymers studied start to decompose rapidly (in air and N_2) above 300-350°C. Thermostability does not depend on Pr concentration and copolymer molecular weight, but it is noticeably affected by the nature of the comonomer, with Pr-DMM being the most and Pr-VAc copolymers being the least thermostable.

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Accepted by editor April 5, 1982
Received for publication May 3, 1982