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Synthesis and Characterization of Poly(vinyl Chloride-g-α-Methylstyrene)— A New Thermoplastic Resin. 2

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ABSTRACT

α-Methylstyrene was grafted on PVC using alkylaluminum Et_2AlCl, Et_3Al, and Me_3Al coinitiators and CH_2Cl_2 as solvent or suspending agent. Grafting was shown to be feasible using both solution and suspension techniques. High grafting efficiency and low monomer conversion were obtained using Et_3Al and Me_3Al, while low grafting efficiency but high conversion could be obtained using Et_2AlCl coinitiator. This paper discusses the synthesis, characterization and some mechanical properties of α-methylstyrene grafted PVC.

INTRODUCTION

Cationic grafting of olefins on chlorine-containing polymers like PVC is now a well-established process. Earlier attempts in cationic

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grafting using Freidel-Crafts catalysts such as $AlCl_3$ were less successful due to significant side reactions like backbone degradation and gelation. Use of alkylaluminum catalysts introduced by Kennedy [1] not only helped to greatly reduce the side reactions but also vastly increased efficiency of grafting. Controlled synthesis of a variety of grafts by cationic grafting technique is now a reality.

The modification of poly(vinyl chloride) (PVC) by cationic grafting has been studied by a number of workers. Thus Kennedy [1] initially grafted isobutylene, butadiene, styrene, etc. using alkylaluminum coinitiators. Gaylord and Takahashi [2] similarly grafted butadiene on PVC using Et_2AlCl and a cobalt salt. Abbas and Thame [3] prepared PVC grafts of isobutylene and butadiene and studied their thermal stability in some detail. Trivedi and Ambrose [4] grafted isobutylene and isoprene using a similar system. The purpose of the above studies in modifying PVC was mainly to prepare an internally plasticized and thermally more stable PVC.

The objective of our current study was to prepare a PVC graft which is not only thermally more stable but which also has a greater range of service temperature than PVC. α-Methylstyrene (α-MS) was chosen for grafting due to the higher T_g of Pα-MS (~170°C). This communication reports the synthesis, characterization, and evaluation of poly(vinyl chloride-g-α-methylstyrene) [P(VC-g-α-MS)] in some details. Part of this work was presented at the III International Symposium on PVC in Cleveland in August 1980 [5].

EXPERIMENTAL

All experiments were carried out in a dry-box under nitrogen atmosphere. PVC (FPC 9326, Firestone Plastic Co.), Et_2AlCl, Et_3Al, and Me_3Al (Ethyl Corp.) were used without further purification. α-MS, THF, CH_2Cl_2, benzene, and hexane (Matheson, Coleman and Bell) were purified in the usual way.

Solution as well as suspension grafting were carried out. For solution grafting, PVC was dissolved in CH_2Cl_2 in a sealed bottle at 50°C and the solution was then transferred inside the dry-box to a three-necked flask at room temperature. The required quantities of α-MS were added to it. At the desired temperature, Et_2AlCl solution was dropwise added using a syringe under vigorous stirring. Second addition, when necessary, was carried out 10 min. after the first addition. At the end of the reaction time, 5 mL MeOH was added to quench the reaction and the product was precipitated in excess MeOH, filtered, and dried in a vacuum oven at 60°C. Grafting efficiency, % α-MS grafted of the total α-MS polymerized, was determined using benzene solvent in a Soxhlet apparatus.

For suspension grafting, PVC was suspended in a mixture of CH_2Cl_2 and α-MS. Alkylaluminum solution was added dropwise using a syringe at the desired temperature. At the end of reaction, 5 mL MeOH was added and subsequently the entire mixture was poured into excess benzene to remove unreacted α-MS and homo-Pα-MS. The mixture was stirred for 30 min and the graft product was filtered and dried as above. The grafting efficiency was % α-MS grafted of the total α-MS polymerized.

Intrinsic viscosity was determined using THF solutions at 24°C in a Ubbelohde viscometer. Gel permeation chromatographs were obtained using THF solutions and a Waters Associate GPC model No. 200.

The relative molecular weights were calculated from the universal calibration curve. The number-average molecular weight of Pα-MS was determined using a Hewlett-Packard high speed membrane osmometer model No. 502 and toluene solvent at 23°C.

Thermal analysis of homo and graft polymers was carried out using DuPont's Differential Thermal Analyser (DTA) model No. 900 and Thermogravimetric Analyser (TGA) model No. 910.

Evaluation of mechanical properties of these copolymers was carried out by first thoroughly mixing them with 1 part Cd/Ba stabilizer and 1 part calcium stearate lubricant, milling on a two-roll mill at 300°F and subsequently molding at 350°F for about 10 min. The molded samples were analyzed for Rockwell hardness and heat distortion temperature according to standard ASTM methods.

RESULTS AND DISCUSSION

Synthesis of P(VC-g-α-MS)

Degradation Study

Controlled experiments using solutions of PVC in CH_2Cl_2 in the absence of monomer established that there were negligible side reactions like degradation or gelation when Et_2AlCl was used. The loss of about 1.6% chlorine can be explained as due to alkylation of labile chlorine by Et_2AlCl. Table 1 gives the results.

Solution Grafting of α-MS

Table 2 shows the results obtained using solution grafting technique. The important conclusions were:

1. α-MS conversions remained somewhat low at -30 and -40°C, but increased significantly at -50 and -55°C.
2. The nature of the Et_2AlCl addition sequence had a profound effect on the α-MS conversion. Thus, adding Et_2AlCl incremently significantly increased α-MS conversion.

It seems that the impurities present in the system act as poisons lowering the overall conversion. Only when these are efficiently

TABLE 1. Effect of Et_2AlCl Reaction on Chlorine Content and Molecular Weight of PVC[a]

PVC sample	Chlorine (wt%)	$[\eta]$ (dL/g)	$\overline{M}_n \times 10^3$	$\overline{M}_w$ (GPC)
Virgin	56.06	0.96	47	124
MeOH precipitated	56.13	0.94	34	127
Virgin/Et_2AlCl treated	54.42	0.96	35	127

[a] PVC = 100 g, CH_2Cl_2 = 300 mL, Et_2AlCl = 2.1×10^{-2} M. Temperature = 40°C. Time = 30 min.

TABLE 2. Solution Grafting of α-MS on PVC Using Et_2AlCl[a]

PVC (g)	CH_2Cl_2 (mL)	α-MS (M)	Et_2AlCl ($M \times 10^2$)	Temperature (°C)	α-MS conversion (%)
5	300	1.30	4.4	-30	1
10	300	1.13	4.4	-40	3
10	300	0.81	4.2	-50	17
10	300	1.10	4.2	-55	11
20	600	1.10	4.2 + 1.9	-55	52
20	600	1.10	2.1 + 4.2	-55	97

[a] Reaction time = 90 min.

scavenged by the use of lower temperatures (slow initiation) or incremental addition of Et_2AlCl can higher conversions become feasible.

Suspension Grafting of α-MS

Data obtained in suspension grafting using Et_3Al and Me_3Al coinitiators are given in Table 3. Grafting efficiencies were extremely high, even using as high a temperature as -10°C. However, α-MS conversion remained very low and therefore incorporation of α-MS in the graft beyond 25% was not feasible.

Some representative data obtained in suspension grafting using Et_2AlCl are given in Table 4. It was found that increased monomer conversion could be brought about by decreasing the reaction temperature or increasing the PVC or Et_2AlCl concentrations.

TABLE 3. Suspension Grafting of α-MS on PVC Using Et_3Al and Me_3Al[a]

PVC (wt%)	α-MS (M)	R_3Al (M × 10^{12})	Temperature (°C)	α-MS conversion (%)	Pα-MS in graft (wt%)	Grafting efficiency (%)
			Et_3Al			
15	4.5	8.6	-40	3.1	9.1	80.4
15	4.5	17.3	-40	5.9	17.7	90.7
15	4.5	17.3	-30	-	6.4	-
10	4.7	15.8	-10	4.4	17.4	78.8
			Me_3Al			
10	4.7	15.9	-10	3.4	14.5	83.3
10	4.7	31.8	-10	5.9	22.0	79.4
10	3.6	24.4	-10	5.4	22.7	90.2

[a] CH_2Cl_2 = 100 mL. Reaction time = 60 min.

TABLE 4. Suspension Grafting of α-MS on PVC Using Et_2AlCl[a]

PVC (wt%)	α-MS (M)	Et_2AlCl (M × 10^2)	Temperature (°C)	α-MS conversion (%)	Pα-MS in graft (wt%)	Graft efficiency (%)
10	5.0	13.8	-35	5	18	28
10	4.7	11.4	-40	7	24	79
10	4.7	15.9	-40	13	32	57
10	4.7	22.7	-40	22	49	72
15	4.5	2.1	-40	17	12	20
18	3.9	3.8	-45	44	10	9
20	3.1	4.5	-60	96	64	-

[a] CH_2Cl_2 = 100 mL. Reaction time = 90 min.

Interestingly, in the suspension system while higher conversions are obtained using Et_2AlCl coinitiator, the grafting efficiencies are always lower than those obtained using Et_3Al or Me_3Al coinitiator systems. The somewhat wide variation in grafting efficiency is possibly because, at higher conversion of α-MS, it was difficult to separate graft polymer from Pα-MS simply by dissolving the latter in benzene at ambient temperature.

In general, however, α-MS grafting on PVC was beset with these problems of low conversion or low grafting efficiency. The graft products separated from homo-Pα-MS could be obtained and further characterized but lengthy extraction procedures were required when Et_2AlCl coinitiator was used for grafting. The lower grafting efficiency with Et_2AlCl system was rather unexpected based on a prior fundamental study of a similar but isobutylene-based polymerization. It clearly showed that t-BuCl/Et_2AlCl system would facilitate termination rather than monomer transfer [6]. Thus, use of Et_2AlCl for grafting on PVC was expected to yield higher grafting efficiency. This assumption, however, is now challenged in the light of a recent study by Trivedi et al. [7, 8]. They have shown that for α-MS polymerization using t-BuCl/Et_2AlCl/CH_2Cl_2, the most probable molecular weight controlling events are temperature dependent in the following way:

Transfer to monomer (0 to -40°C)
Termination (-40 to -63.5°C)

Since our above study was carried out using temperatures higher than -45°C, transfer to monomer might be rather prominent, resulting in the low grafting efficiency.

Apparently, for Et_3Al and Me_3Al systems, the termination is so efficient that while high grafting efficiencies are indeed obtained, the conversion remains fairly low. These results suggest that a highly controlled grafting mechanism is operative which includes an effective initiation at the PVC backbone and efficient termination of growing chains by counteranion $R_3AlCl^{\ominus}$.

Characterization of P(VC-g-α-MS)

GPC Study

GPC curves for selected samples prepared in solution at -55°C (52% conversion, Table 2) are shown in Fig. 1. The extracted graft samples contained 37% Pα-MS grafted. The following conclusions can be drawn from this study about the extracted graft copolymer:

1. GPC for graft copolymer is a monomodal, which suggests that most probably the grafting reaction is quite uniform. The product therefore is indeed a graft copolymer and not just a mixture of two homopolymers.
2. Extracted graft sample elutes at lower GPC count than PVC. This suggests it has a higher molecular weight than PVC. This again confirms that grafting is indeed taking place.

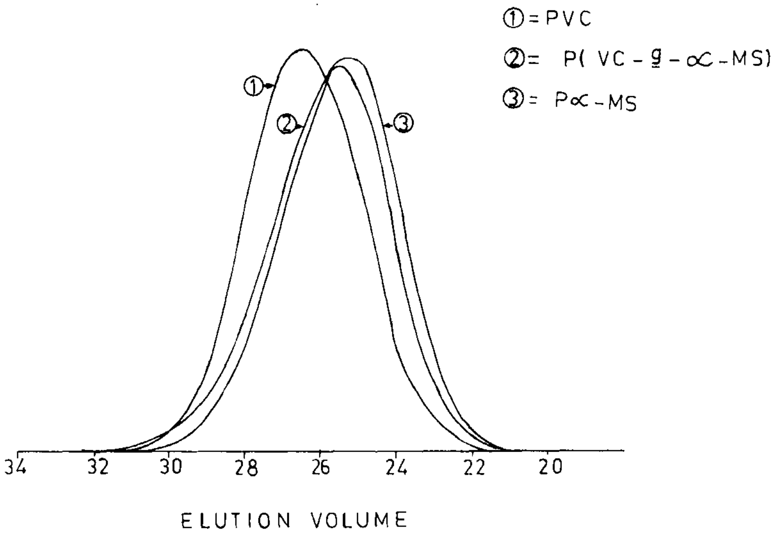

FIGURE 1.

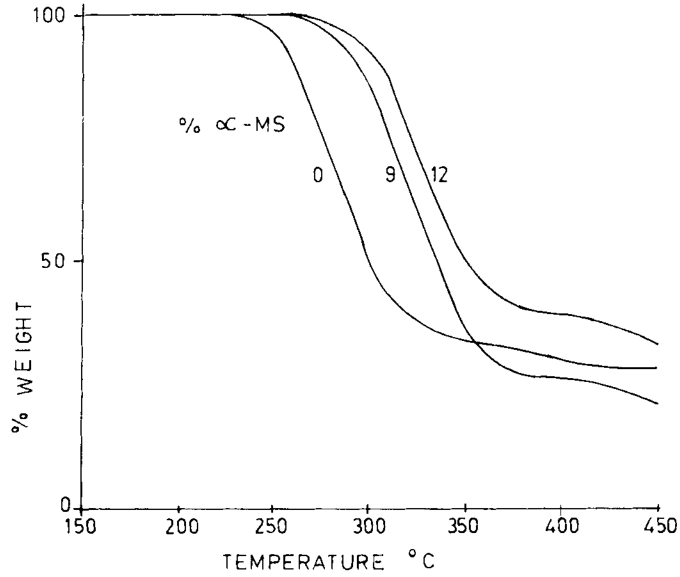

FIG. 2. TGA of PVC and P(VC-g-α-MS).

TABLE 5. Mechanical Properties of PVC Grafts and Blends

Pα-MS (wt%)	HDT °C (66 psi)	Rockwell hardness (M)
Grafts		
4.8	78	69
25	83	79
37	116	88
66	131	Too brittle
Blends		
25	84	61
50	87	57
PVC Control	82	68
Chlorinated PVC	119	47[a]

[a] Rockwell E scale.

Similar conclusions were arrived at for P(VC-g-α-MS) prepared using suspension grafting process.

Thermal Analysis

DTA was carried out to determine the glass transition temperature, T_g, of homo and graft copolymers. Interestingly, T_g of Pα-MS depended significantly on the molecular weight of the polymer. Thus, T_gs of Pα-MS were 167, 155, and 127°C with the corresponding number-average molecular weights as obtained by osmometry being 30,000 (Et_2AlCl system/solution), 17,000 (Me_3Al system/suspension), and 11,000 (Et_3Al system/suspension).

For the unextracted graft products prepared in solution (Et_2AlCl system) containing 29, 37, and 72% Pα-MS, two T_gs were observed; 83 and 143°C. Similar result was obtained for a Soxhlet-extracted graft sample which contained 37% grafted Pα-MS. On the other hand, the extracted homo Pα-MS showed a high T_g of 167°C. These results seem to suggest that a marginal compatibility does exist between PVC and Pα-MS which decreases the T_g of Pα-MS. It is, however, not clear why T_g of PVC is not affected. Direct electron micrograph evidence may help clear the above anomaly.

On the other hand, TGA clearly shows that the thermal stability of PVC improves significantly even when small quantities of α-MS are grafted (Fig. 2). Thus, for example, while 50% weight loss occurred at 310°C for a controlled PVC sample, the corresponding loss was less than 15% for graft copolymers containing 10 and 40% Pα-MS. Apparently the removal of labile chlorine from PVC by grafting α-MS, as was also the case with other monomers [1], results in significant improvement in the thermal stability.

Mechanical Properties

Table 5 gives the heat distortion temperature (HDT) and hardness of the extracted graft samples and PVC/Pα-MS blends. Data for control PVC and a chlorinated PVC are also given for comparison. It seems that a low percentage of grafting tends to reduce the heat distortion temperature somewhat. However, a heat distortion temperature approaching that of chlorinated PVC can be obtained for graft products containing about 37% grafted Pα-MS. While HDT can possibly be further increased by increasing the Pα-MS content of the graft, the products with high Pα-MS content tend to become very brittle and are difficult to mold and process.

The blending of PVC and Pα-MS on a two-roll mill and subsequent molding of blends showed only marginal improvement in HDT and a drop in hardness. Apparently the low compatibility of PVC and Pα-MS does not allow formation of a strong matrix required for significant enhancement in mechanical properties.

CONCLUSION

Grafting of α-MS on PVC can be carried out using R_3Al or Et_2AlCl coinitiator systems. Either solution or suspension systems can be used. The graft products show a significant increase in thermal stability and mechanical properties, though their processibility seems to suffer in comparison to those of rigid PVC.

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