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Synthesis and Properties of Poly(Vinyl Chloride-g-2-Methyl-2-Oxazoline)

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SUMMARY

Poly(vinyl chloride-g-2-methyl-2-oxazoline) copolymers were prepared by grafting from the allyl chloride sites of PVC with KI or $AgOSO_3CF_3$ as coinitiators. Use of $AgOSO_3CF_3$ led to higher grafting efficiencies and higher contents of poly(2-methyl-2-oxazoline) in the graft copolymers. DTA analyses of the P(VC-g-Me-Oxz) identified the thermal transitions of this copolymer; TGA analyses showed that the graft copolymers were less thermally stable than the constituent homopolymers. Unlike blends of P(Me-Oxz) and PVC, the graft copolymers could be molded easily; the graft materials exhibited greater flexural moduli but lower HDT's than PVC.

INTRODUCTION

The homopolymerization of 2-substituted-2-oxazoline using cationic initiators has been reported by various workers (TOMALIA and SHEETS, 1966, KAGIA, et al. 1966, BASSIRI et al. 1967). SAEGUSA et al. studied the alkyl iodide (1973a, 1973b, 1973c) and the benzyl chloride (1976) initiated homopolymerization of 2-methyl-2-oxazoline (Me-Oxz) in detail. He (1975) also grafted 2-methyl-2-oxazoline from chloromethylated polystyrene using potassium iodide as the coinitiator. More recently, TOMALIA and ZUBRITSKY (1978) claimed the use of allyl chloride, or preferably vinyl benzyl chloride (optionally with sodium iodide as coinitiator) to homopolymerize Me-Oxz. Similarly, SAEGUSA et al. (1978) found that the macromolecular allyl chloride, 1-chlorobutadiene-butadiene copolymer, could be used for grafting Me-Oxz.

The small concentration of allylic chlorine atoms present in poly(vinyl chloride), PVC, has been successfully utilized in conjuction with specific coinitiators for certain grafting reactions. For example, the

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PVC/Et_2AlCl combination was found to be an excellent initiating system for polymerizing isobutylene (KENNEDY and DAVIDSON, 1977) and styrene (KENNEDY and NAKAO, 1977). The PVC/$AgOSO_2CF_3$ macroinitiator proved useful for grafting polyethers from PVC. (DREYFUSS and KENNEDY, 1976, 1977).

By judiciously cross-fertilizing the chemistry of Me-Oxz with that of PVC, we have synthesized novel poly(vinyl chloride-g-2-methyl-2-oxazoline) copolymers. This paper describes a preliminary study of the preparation and properties of such materials.

EXPERIMENTAL

MeOxz (Aldrich) was distilled twice over Molecular Sieves Type 3A (Linde Div.) and also stored over it. DMF (Fisher) was similarly purified. CH_2Cl_2 (Matheson Coleman Bell) was distilled and stored over CaH_2, while THF (Fisher) was used as received. PVC (FPC 9300) was dried in a vacuum oven for 2 hours at 60°C and subsequently cooled and transferred to a bottle under nitrogen in a stainless steel dry box. KI (Fisher) and $AgSO_3CF_3$ (Ozark Mohoning) were dissolved respectively in DMF and THF and the desired amounts of them were added last to the reaction mixture. All transfers were carried out under nitrogen atmosphere.

Poly(vinyl chloride-g-2-methyl-2-oxazoline) copolymers were prepared by dissolving PVC in CH_2Cl_2 or DMF solvent or in 2-methyl-2-oxazoline monomer (bulk) in sealed beverage bottles. Coinitiators, if any, were added and the bottles rotated in a polymerization bath at 80°C. At the end of the desired reaction time, the bottles were cooled, opened and the contents were poured into a large excess of MeOH with constant stirring. For very viscous solutions or for semisolid polymers, first DMF was added to the reaction mixture to dilute the solution and subsequently the product was precipitated in MeOH. The precipitate was left standing in MeOH at least overnight before filtering and drying. Since homo poly(MeOxz) is soluble in MeOH, it was possible to separate it from the graft and PVC by this technique.

Poly(2-methyl-2-oxazoline) homopolymers were prepared according to modifications of existing methods (TOMALIA and ZUBRITSKY,1977) Allyl chloride was used as the initiator and DMF was used as the solvent. The polymerizations were run at 80°C.

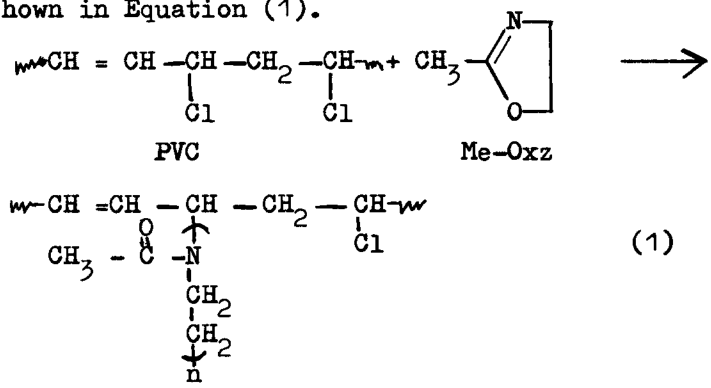
Differential Thermal Analyses (DTA) were carried out using a DuPont model No. 900 instrument under nitrogen atmosphere and a heating rate of 20°C/min.

Thermal Gravimetric Analyses (TGA) were performed with a DuPont Model No. 910 instrument under a nitrogen atmosphere and a heating rate of 10°C/min.

The milling of the graft materials was carried out at 140°C, after mixing it with 1 phr calcium stearate (Fisher) and calcium-barium laurate (Fisher). Subsequently, molding was carried out at 170°C for up to 10 minutes. The molded samples were analyzed for Heat Distortion Temperature (HDT) at 66 psi pressure (ASTM D-648) and flex properties (ASTM D-790).

RESULTS AND DISCUSSION

The graft polymerization that we examined is shown in Equation (1).



(1)

P(VC-g-MeOxz)

Preliminary experiments showed negligible grafting in the absence of coinitiators. Hence, the coinitiators KI and AgSO$_2$Cl were tried. (Tables I and II). The KI coinitiator had previously been used to facilitate grafting of MeOxz from chloromethylated polystyrene (SAEGUSA, 1975). AgSO$_3$CF$_3$ was the coinitiator of choice for grafting polyethers from PVC (DREYFUSS and KENNEDY, 1976,1977).

The grafting processes were carried out using CH$_2$Cl$_2$ or DMF as solvents or in bulk (Me-Oxz the solvent). The inadequacy of the solvent methods is clearly shown in Table I, where grafting efficiencies are substantially low.

In contrast, the bulk system was not only convenient but also led to high grafting efficiencies (Table I). However, as the bulk grafting reaction progressed, the viscosity of the medium increased significantly. After about 17% conversion, the reaction mixture became semi-solid, due to absorption of monomer by the graft copolymer, limiting further polymerization. Both the conversion and the poly-

TABLE I

SYNTHESIS OF POLY (VINYL CHLORIDE-g-Me-Oxz) USING KI COINITIATOR AT 80°C.

Grafting Conditions	Time hrs.	Conversion %	P(Me-Oxz) In Graft % Wt.	Grafting Efficiency %
CH_2Cl_2 Sol.	109	43	13	12
DMF Sol.	160	34	22	12
Bulk	72	8	31	41
Bulk	96	14	43	41
Bulk	120	12	58	81
Bulk	160	17	61	69

KI = 1.5 mmole for all experiments

CH_2Cl_2 solution: PVC=20 gms, Me-Oxz=55 ml
CH_2Cl_2 = 600 ml
DMF solution: PVC=15 gms, Me-Oxz =100 ml,
DMF = 100 ml
Bulk: PVC = 15 gms, Me-Oxz = 200 ml.

TABLE II

SYNTHESIS OF POLY (VINYL CHLORIDE-g-Me-Oxz) USING $AgSO_3CF_3$ COINITIATOR AT 80°C IN BULK

Time	Conversion %	P(Me-Oxz) In graft, % Wt.	Grafting Efficiency,%
15	2.6	15.7	53.8
20	3.1	21.9	68.8
39	6.5	44.9	93.8
47	9.7	51.6	82.8

PVC = 15 gms, Me-Oxz = 200 ml, $AgSO_3CF_3$=0.39 mmoles

(Me-Oxz) content in the graft increased with reaction time, (Tables I, II). However, the grafting efficiency vs. time response was not linear; there was a sharp increase in grafting efficiency part way into the reaction period, followed by a decrease in grafting efficiency. This type of behavior might be due to inhibition of the polymerization by impurities very early in the reaction and competing chain transfer processes very late in the reaction. An alternate explanation for the lowering of grafting efficiency late in the reaction period might be that thermal degradation of the PVC produces HCl which initiates the homopolymerization of Me-Oxz (SAEGUSA, 1978).

$AgSO_3CF_3$ was found to be a much more effective coinitiator than KI for graft copolymerizations with Me-Oxz (Table I vs. Table II). Higher conversions were obtained for the $AgSO_3CF_3$ coinitiated systems, even at 1/5 the coinitiator concentrations of the KI coinitiated processes. Also, use of $AgSO_3CF_3$ resulted in higher grafting efficiencies and greater poly (Me-Oxz) contents in the graft copolymers than in the case of KI coinitiated reactions.

It is believed that the Ag^+cation enhances P(Me-Oxz) initiation by the formation of AgCl precipitate. In addition, the $SO_3CF_3^-$ anion is expected to propagate faster than the I^- anion because $SO_3CF_3^-$ is less nucleophilic than I^- (SAEGUSA, 1976).

While a study of the molecular weights of the poly(vinyl chloride-g-2-methyl-2-oxazoline) copolymers was made difficult because of the sparse solubility of these materials, they were amenable to thermal analyses. The DTA thermograms of these copolymers exhibited complex thermal transitions, as described in Table III.

The Tg of the poly(Me-Oxz) backbone (-81°C), its side chain (50°C) and the Tm of poly(Me-Oxz)(130°C), as well as the Tg of PVC (80°C) are readily identifiable. A comparison of DTA data (Table III) with TGA data (Fig. 1) suggests that the peaks at 245,285,and 350°C may represent PVC degradation and/or P(Me-Oxz) degradation or cyclization. Also of interest is the fact that the Tg of the PVC backbone and the Tg of P(Me-Oxz) graft are nearly the same as the constituent homopolymers. This lack of compatibility between the PVC backbone and the P(Me-Oxz) branches may possibly be due to crystallization of the P(Me-Oxz) branches.

TABLE III

DTA THERMAL TRANSITIONS OF HOMOPOLYMERS AND GRAFTS

Exp. Temp., °C	Lit. Temp., °C	Type of Transitions
Poly(2-methyloxazoline)		
-81	-	P(Me-Oxz) backbone Tg
50-80	80[1]	P(Me-Oxz) sidechain Tg
150-200	200[1]	P(Me-Oxz) Tm
375	-	P(Me-Oxz) degradition (?)
Poly(vinyl chloride)		
-	81[2]	PVC Tg
Poly(vinyl chloride-g-Me-Oxz)		
-81	-	P(Me-Oxz) backbone Tg
50	-	P(Me-Oxz) sidechain Tg
80	-	PVC Tg
130	-	P(Me-Oxz) Tm
245,285,350	-	P(VC-g-Me-Oxz) cyclization, degradation (?)

[1] Ref. 1, [2] Ref. 2

Fig. 1 also compares the thermal stabilities of PVC and P(Me-Oxz) homopolymers with two poly(vinyl chloride-g-2-methyl-2-oxazoline) copolymers. The hygroscopic P(Me-Oxz) homopolymers lose about 10% of their weight between 100-200°C, in part, by loss of water. Yet, the P(Me-Oxz) homopolymer is generally more stable (30% weight loss at 375°C) than PVC (30% weight loss at 325°C). Despite these facts, the graft copolymers are less stable (30% weight losses at 195, 270°C) than either of the homopolymers. The reduced stability of the graft copolymers may be due to accelerated HCl loss by P(Me-Oxz) or catalyst residues (GUPTA et al., 1978).

Preliminary studies of the mechanical properties of PVC, P(Me-Oxz), blends of PVC and P(Me-Oxz) and poly(vinyl chloride-g-2-methyl-2-oxazoline) were carried out. It can be seen that neither poly(2-methyl-2-oxazoline) homopolymer or a PVC/P(Me-Oxz) blend gave satisfactory properties. Both materials were too brittle to test (Table IV).

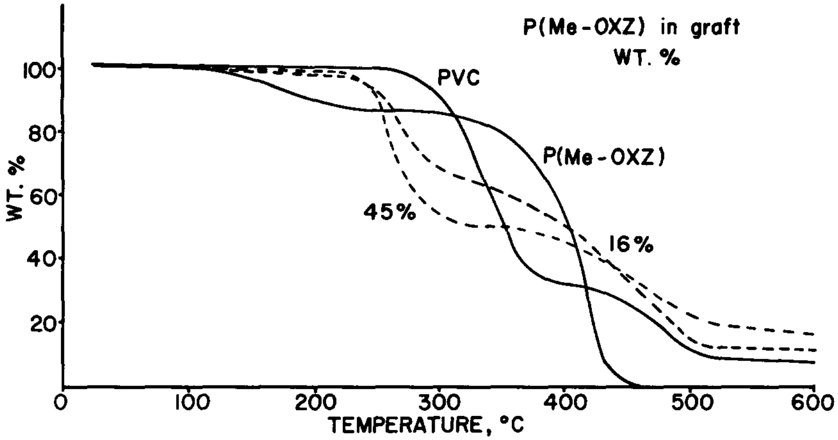


Figure 1: TGA plots for PVC, P(Me-Oxz) and two P(VC-g-Me-Oxz) copolymers with 16% and 45% P(Me-Oxz)

TABLE IV

MECHANICAL PROPERTY STUDY OF P(VINYL CHLORIDE-g-Me-Oxz)

Co-initiator Used	P(Me-Oxz)	Flex Modulus	Flex Str.	Remarks
Graft	% wt.	psi	psi	
KI	51	467000	7100	Could easily be molded
$AgSO_3CF_3$	35	502000	5300	
$AgSO_3CF_3$	60	527000	4200	
Blend				
Allyl Chloride	50	-	-	Extremely brittle
P(Me-Oxz)				
Allyl Chloride	100	-	-	Extremely brittle
PVC				
	0	395000	11000	Does not break

In contrast, the P(VC-g-Me-Oxz) copolymers could be easily molded and exhibited flexural moduli higher than that of PVC itself (Table IV). However, the flexural strengths of the copolymers were lower than that of PVC. This result suggests that P(Me-Oxz) behaves as a nonreinforcing filler for PVC. Also, despite the fact that the Tm of P(Me-Oxz) is higher than the Tg of PVC, grafting P(Me-Oxz) from PVC lowers the heat distortion temperature (HDT) of

PVC (Table V). Apparently, the Tg of P(Me-Oxz) has a greater effect on material HDT than the Tm of P(Me-Oxz). However, the amount and quality of graft crystallinity may also be important factors because the HDT's of the graft copolymers increase as the P(Me-Oxz) content of the grafts increases from 35-41%.

TABLE V

HDT OF POLY(VINYL CHLORIDE-g-Me-Oxz)[1]

P(Me-Oxz) In Graft,% wt.	HDT °C
0	82
13	79
35	55
41	65

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[1] HDT samples prepared using KI coinitiator at 80°C.

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