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Cationic Reactions in the Melt
1. The Effect of Lewis Acids on Polystyrene

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SUMMARY

The effect of Lewis acids of different acidities, i.e., $AlCl_3$ and Bu_2SnCl_2, on polystyrene melt has been investigated using the mixing chamber of a Brabender Plastograph at 180°C. The torque was monitored as a function of time and molecular weights of periodically withdrawn samples were determined. The structure of select samples has been analyzed by ^{1}H-NMR spectroscopy. A sequence of complex physical and chemical transformations has been identified. The addition of Lewis acids to polystyrene melts causes an immediate drastic decrease in the torque due to rapid partial polymer degradation which is followed by homogenization and a slower degradation phase. There is evidence for the formation and accumulation of unsaturation during degradation. Cationic reactions induced by the Lewis acids readily explain the observed sequence of chemical transformations.

INTRODUCTION

In the course of our continuing research since many years on the mechanism of cationic polymerihations we have accumulated a large amount of fundamental information by carrying out experiments in the conventional manner, i.e., in stirred reactors and homogeneous solvent systems. However, the use of purified solvents significantly contributes to the cost of running these reactions and render them unattractive on a technological scale. Thus it appeared to be of interest to investigete carbocationic reactions in the bulk or in the melt, in the absence of solvent. Our first specific objective was to attempt grafting of one polymer sequence onto another by generating polymeric carbocations via controlled electrophilic degradation in the melt under shear and to trap these cations by alkylative grafting onto a preformed second polymer in the system.

A literature search undertaken prior to experimentation, provided very little pertinent information. Although a number of publications and monographs concern Friedel-Crafts reactions (THOMAS 1941, OLAH 1963, OLAH 1973), very few were published on the interaction of polymers and Lewis acids. Most of the experiments were carried out in solution and it was established that Lewis acids degrade polymers (FRANK 1963a, CARRICK 1970, PAPIRER et al. 1975) usually producing double bond containing compounds. Attempts have been made to modify polymers by Friedel-Crafts reactions in solutions (FRANK 1963b, GRASSIE et al. 1973, GRASSIE and GILKS 1973, CARRICK 1970, KRAKOVYAK et al.

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1976). Recently experiments in the melt phase have been described (BARAMBOIM et al. 1979). Though the detailed chemistry of these reactions remains obscure the feasibility of Friedel-Crafts modification of polymers has been demonstrated.

This paper describes the first phase of our investigations on the behavior of polystyrene in the presence of a relatively strong and a weak Friedel-Crafts acid, $AlCl_3$ and Bu_2SnCl_2. A series of complex changes in the rheology and molecular weight of the melt have been identified and characterized, and a hypothesis to account for the observations is developed. Subsequent papers in this series will deal with EPM and EPDM/Friedel-Crafts acid systems and graft syntheses in the melt.

EXPERIMENTAL

Polystyrene (Styrene 666 U, Dow Chemical, PSt) anhydrous $AlCl_3$, and Bu_2SnCl_2 (Aldrich Chemical Co.) were used as received. The Lewis acids were weighed and sealed into small (1x1") polyethylene bags under N_2 atmosphere and added to the polymer melt. The weight of the empty bags was 0.1-0.2 wt% of the total charge; the presence of this small amount of polyethylene in the melt did not affect the measurements.

Molecular weights were determined by a high pressure GPC unit (Waters 6000 A, Waters Associates Inc.) equipped with RI and UV detectors. Chemical changes were followed by ^1H-NMR spectroscopy (Varian T 60 NMR Spectrometer).

Reactions were carried out in the mixing chamber of a Brabender Plastograph (C.W. Brabender Instruments Inc.), fitted with cam type blades at 180°C, 50 rpm and 55 g charges. Lewis acids were added after 15 mins of mixing, i.e., after complete fusion and homogenization of PSt. The torque was continuously recorded. Samples were withdrawn at different intervals and were characterized by structure (^1H-NMR) and molecular weight (GPC) determinations.

Samples were purified by dissolution in THF, precipitation into MeOH, and drying in vacuo at room temperature. In some cases very low molecular weight material was recovered by solvent evaporation.

RESULTS AND DISCUSSION

Figure 1 shows representative torque versus time profiles obtained in experiments in which $AlCl_3$ or Bu_2SnCl_2 was added to PSt melts. The addition of Lewis acids (LA) induces a series of complex chemical reactions which cause characteristic changes in the flow-properties of the melt. An examination of the torque versus time profile suggests the following phases:

A-B: Melting of PSt and temperature stabilization.

at B: The LA is added; the torque drops immediately and drastically due to rapid degradation of a small amount of PSt to very low molecular weight material.

B-C: The torque rises during homogenization of the low molecular weight material with the melt matrix.

at C: The melt is homogeneous: mixing is complete.

C-D: The torque decreases due to homogeneous cationic chain scission in the melt.

D-E: The torque slowly increases due to slow, molecular weight increasing processes.

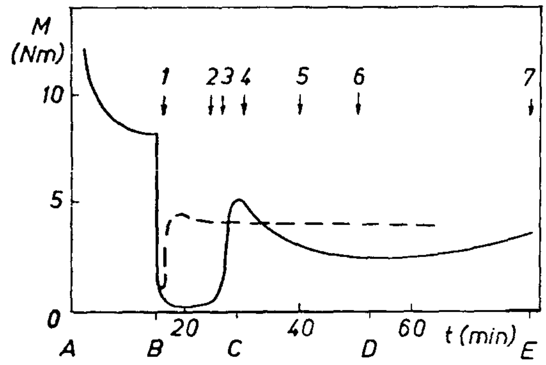
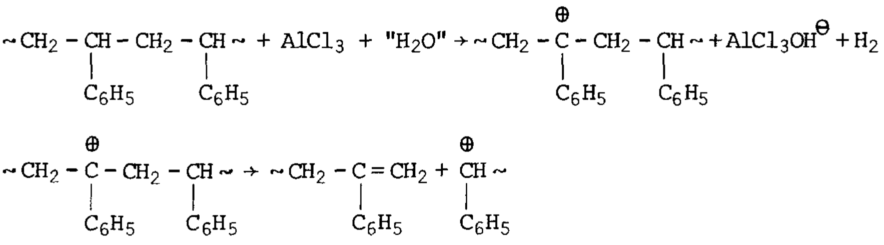


Figure 1. Representative torque vs time traces of PSt/$AlCl_3$ (0.63 g) and PSt/Bu_2SnCl_2 (3.77 g, dotted line) experiments. The letters and numbers indicate reaction stages and sampling points, respectively, with reference to the PSt/$AlCl_3$ experiment.

The following discussion amplifies these statements and provides a hypothesis to account for the observations. Essentially the same phenomena have been observed with $AlCl_3$ and Bu_2SnCl_2, however, the effects are less pronounced with the weaker Lewis acid.Even at higher Bu_2SnCl_2 concentrations the final, slow molecular weight increase is absent, i.e., phase C-E is horizontal.

Evidently the degradation of PSt upon the addition of Lewis acids is immediate under our reaction conditions. As soon as the $AlCl_3$ contacts the PSt melt extensive chain cleavage occurs, conceivably by the following cationic process:



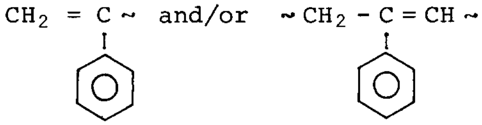
$$\sim CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}\sim + AlCl_3 + "H_2O" \rightarrow \sim CH_2-\underset{C_6H_5}{\underset{|}{\overset{\oplus}{C}}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}\sim + AlCl_3OH^{\ominus} + H_2$$

$$\sim CH_2-\underset{C_6H_5}{\underset{|}{\overset{\oplus}{C}}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}\sim \rightarrow \sim CH_2-\underset{C_6H_5}{\underset{|}{C}}=CH_2+\underset{C_6H_5}{\underset{|}{\overset{\oplus}{CH}}}\sim$$

Adventitious moisture (indicated by quotation marks) in conjunction with $AlCl_3$ may form the hypothetical acid $H^{\oplus}AlCl_3OH^{\ominus}$ which effects hydride-abstraction, and the transitory benzyl cation induces β cleavage. While the extent of degradation in terms of chain scission (molecular weight and torque decrease) is substantial, the amount of degraded polymer is limited to the vicinity of contact between the introduced $AlCl_3$ and PSt. The small amount of very low molecular weight PSt tends to coat the mixing head and acts as a lubricant for the rest of the melt. During phase B-C the system undergoes homogenization by mixing and diffusion of the very low molecular weight PSt with the largely unchanged matrix of the melt. The torque remains low as long as the low molecular weight PSt adheres to the mixing head, and the length of this phase is affected mainly by the amount of Lewis acid added.

At C the torque reaches a maximum most likely because at this point the homogenization of the low molecular weight PSt and the rest of the melt is complete.

The formation of the low molecular weight product was confirmed by visual observation (appearance of a film adhering to the mixing blades) and by molecular weight determination of a sample taken at the minimum torque (Sample 1, Figure 1). According to GPC, the $\bar{M}_n$ of this sample is between 700 and 8000. This fraction exhibits strong UV intensity at 254 nm (Figure 2, sample 1) and its ^{1}H-NMR spectrum (Figure 3 b) suggests the presence of unsaturation conjugated with aromatic ring (resonance at 5.3 ppm):



$CH_2 = C(C_6H_5){\sim}$ and/or ${\sim}CH_2 - C(C_6H_5) = CH{\sim}$

Experiments have been carried out in which the molecular weights of samples withdrawn at various key points during a run have been determined. Table I shows the overall molecular weights of samples 1-7 (for sample withdrawal times see Figure 1). Evidently the overall $\bar{M}_n$ first drops precipitously (from 111.5×10^3 to 15.5×10^3) upon $AlCl_3$ addition and after reaching a minimum at 12.4×10^3, it rapidly increases (30.7×10^3). This trough formation reflects the minimum formed in the B-C phase in the torque vs. time profile and is attributed to the formation of the very low molecular weight "plasticizer" around the mixing blades and its homogenization with the largely unchanged melt matrix. Degradation of the homogeneous melt progresses and the $\bar{M}_n$ decreases again (23.1×10^3). Finally branching and crosslinking commences which causes an increase in $\bar{M}_n$(33.1×10^3). These changes reflect those observed in the torque vs. time traces.

The final $\bar{M}_n$ increase in phase D-E may not be due to ring alkylation. If ring alkylation were important, there would be two possibilities regarding the course of the PSt/LA interaction. If alkylation were fast the molecular weight would increase earlier than observed. If degradation were much faster the polymer would degrade to a very low molecular weight product and the molecular weight would not increase during the after-homogenization phase. The delayed increase in molecular weight may be due to double bonds formed during degradation or by H abstraction.

The formation of double bonds is demonstrated by the high UV absorption of the small molecular weight fractions (Fig.2.) and by their NMR spectra (Fig.3.) This proposition is further corroborated by the fact that the same kind of torque (molecular weight) increase was observed with ethylene-propylene copolymer as well (PUKANSZKY et al. 1981) although ring alkylation could not have taken place with this polymer. The molecular weight increase may be due to a reaction between carbocations and double bonds formed during degradation.

Table I.

Molecular weight changes during the PSt/AlCl$_3$ experiment (180°C, 50 rpm, 55 g charge, 0.636g AlCl$_3$)

Sample No.*	Overall molecular weights		Molecular weight of high molecular weight fraction**	
	$\bar{M}_n$ x 10^{-3}	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ x 10^{-3}	$\bar{M}_w/\bar{M}_n$
Styrene 666 U	111.5	2.4		
1	15.5	9.7	77.5	2.4
2	12.4	12.0	91.6	2.0
3	16.1	9.6	96.0	2.1
4	20.9	6.7	93.9	2.2
5	30.7	4.4	68.5	2.3
6	23.1	5.2	44.7	2.8
7	33.1	3.7	44.1	2.9

* The arrows in Figure 1 indicate the time of sample withdrawal
** Obtained from the high molecular weight part of the GPC trace

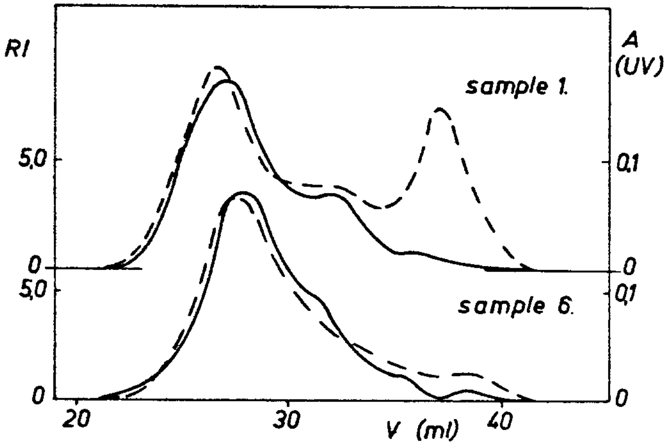


Figure 2. GPC trace of samples taken from the mixing chamber; —— refractometer, --- UV absorbance (254 nm) trace

To further confirm our assumptions the concentration of chain-end double bonds was calculated and plotted against time (Fig.4.). To achieve this the molecular weight versus torque relationship has been determined (Fig.5.) and the number of double bonds (p$^{\ominus}$) was calculated from the measured torque data by:

$$p^{\ominus} = S - C = \frac{\bar{M}_{n,o}}{\bar{M}_n} - 1$$

where S is the average number of scissions and C is the average number of crosslinks. $p^\ominus$, S and C are all related to one original macromolecule. The above equation is valid because chain-end double bonds are formed during chain scissions and consumed during crosslinking; consequently $p^\ominus$ always reflects the actual amount of double bonds present in the polymer.

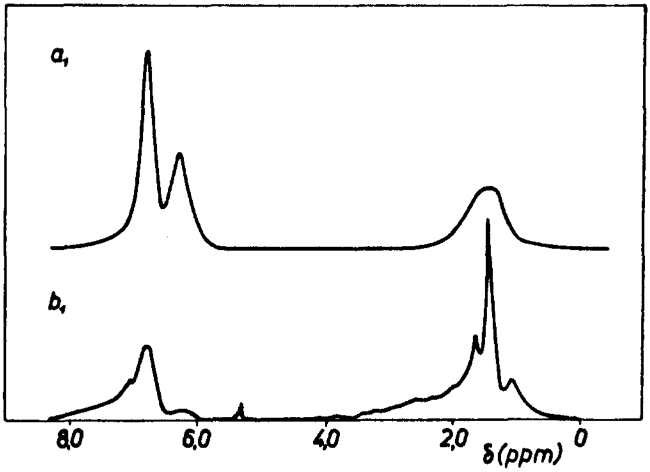


Figure 3. NMR spectra of a) Styrene 666 U, and b) low molecular weight fraction

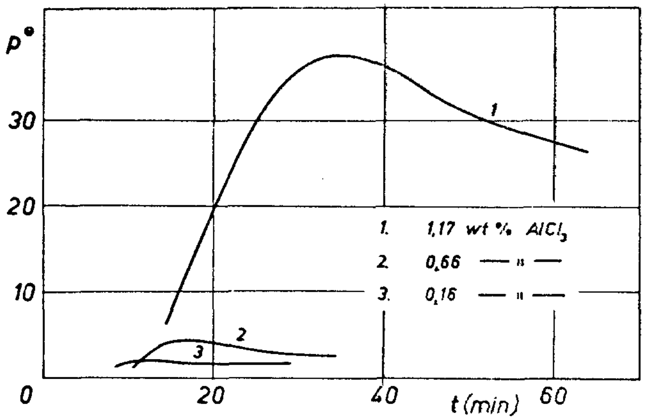


Figure 4. Dependence of $p^\ominus$ (number of double bonds) on mixing time in the PSt/$AlCl_3$ system at different $AlCl_3$ concentrations (wt.%)

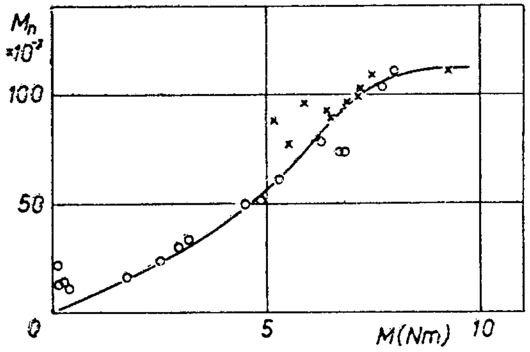


Figure 5. Empirical correlation between torque and number average molecular weight (by GPC) of PSt at 180°C

After homogenization first the number of chain scissions increases rapidly and then it slows down. This complex phenomenon may be due to a variety of illdefined degradation-branching-crosslinking events occuring at various rates.

The effect of LA concentration on $p^{\ominus}$ is shown in Fig.6, where the maximum number of double bonds ($p^{\ominus}_{max}$) is plotted against the LA concentration. With increasing LA concentration the probability of degradation increases, thus the accumulation of chain-end double bonds may increase before alkylation becomes predominant.

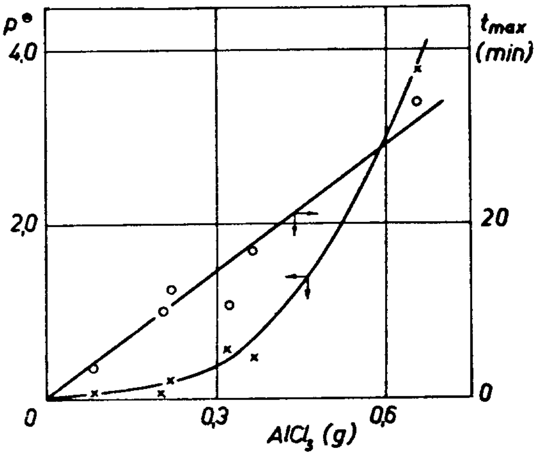


Figure 6. Dependence of $p^{\ominus}_{max}$ and t_{max} on $AlCl_3$ concentration (wt.%)

In contrast to the complicated torque vs. time profiles observed with $AlCl_3$, those arising with Bu_2SnCl_2 appear to be much simpler. A sharp drop occurs upon the addition of this weak Lewis acid also, however, the homogenization phase is very short and after homogenization of the melt the torque does not change. The carbocationic reaction chain might be rapidly terminated by hydridation or butylation (KENNEDY and RENGACHARY 1974); however, the drop in the torque may also be due to the lubricating effect of the considerable amount of Bu_2SnCl_2 present in the melt (3.77 g).

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