

Acylation Reaction of Polystyrene with Organic Anhydrides and Investigation of the Physico-Mechanical Properties

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Abstract

The acylation reaction of polystyrene with organic anhydrides, such as maleic and acetic anhydrides were investigated in the presence of cationic catalysis (AlCl_3 , $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, FeCl_3 , SnCl_4 , TiCl_4 , ZnCl_2), to synthesise some polyfunctional (carbonyl-, carboxyl-, keto-, olefinic) polystyrene. The incorporation of functional groups to polystyrene were caused an increase of adhesion capability, physico-mechanical properties, elasticity and photosensitivity polyfunctional product.

Introduction

The synthesis of new polymeric materials having complex properties has recently become of great practical importance to polymer chemistry as well as plastic technology. Generally, the synthesizing of new polymeric materials can be prepared by either the polymerization of their monomers or chemical modification of polymers appropriate with in polymer technology, the acylation reaction is very important for producing new polymeric materials from polystyrene polyfunctional groups, in industry [1-6].

Today, polystyrene (PS), which is widely used in industrial applications as polyolefins and polyvinylchlorides, is also used for the production of plastic materials, which are used instead of metals in technology. The acylation reactions, in polymer chemistry, especially to producing of new polymeric materials from PS are very important.

In our earlier work [7-11], the some polyfunctional polystyrenes which were prepared with different functional groups for such as epichlorohydrine, organic anhydrides and unsaturated hydrocarbons, in the presence of cationic catalysis. Therefore, the adhesion capability and corrosion resistance of the obtained polyfunctional products were increased against various type materials, i.e. metals, glass or wood.

In this study, the chemical modification of polystyrenes with maleic anhydride and acetic anhydride were performed in the presence of cationic catalysis.

The prepared polyfunctional polystyrene have different functional groups such as ($-\text{C}=\text{C}-$; $-\text{CO}-\text{CH}_3$; $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$), that the physico-mechanical, thermal, adhesion properties of the polyfunctional polystyrenes were investigated on the nature and the quantity of binding functional groups to the aromatic ring.

In this paper we will briefly summarize all the aspects of the acylation reactions of PS with organic anhydride, and will be covered in previous specialized reviews, allowing for a broad and general discussion on the subject. The chemical modification of PS in the presence of cationic catalysis will be discussed [3-6].

Experimental

Materials

Polystyrene (PS) used was obtained according to emulsion method ($M_n = 5.0 \times 10^5$). Maleic anhydride (MA) used was purified by recrystallization from benzene, followed by sublimation in vacuum, m.p. $52,8^\circ\text{C}$. Acetic anhydride (AA) was used by distillation after dried over Na_2SO_4 , m.p. 140°C ; d_4^{20} : 1,0820, n_D^{20} : 1,3904.

The Lewis acids catalysis as $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, TiCl_4 , SnCl_4 , FeCl_3 , ZnCl_2 and AlCl_3 were commercial products and the all were distilled under nitrogen atmosphere, diluted with chloroform and sealed in glass ampoules.

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Modification

In a 250 mL flask, 5,2 g (0,05 mol) PS and 40 mL of chloroform were mixed and stirred for one hour, then this solution 0,98 g (0,01 mol) of MA (corresponding to 20 mol% MA with respect PS) was added and 1,4 mL the catalysts $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]$ was added dropwise at the same temperature and were stirred for 2 more h. Modified PS was precipitated by methanol from the reaction mixture, filtered and dried under vacuum at 40°C for 5 h. Conversion is found as 6,0 g (97,5 %). The characteristics of the synthesized polymers were as following: T_g (by DCS analysis) 145°C, $[\eta]$ in toluene at 25°C 0,75 dL/g, acid number (AN) 136 mg KOH/g, thermostability (by TGA analysis) 350°C.

The chemical modification of PS with acetic anhydride by using the other catalysts, namely TiCl_4 , AlCl_3 , SnCl_4 , FeCl_3 , ZnCl_2 and FeCl_3 were employed at the same optimum reaction conditions, as achieved for $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$.

The chemical modification of PS with MA were employed at the some optimum reaction conditions obtained for the above. The reaction conditions is as following (PS: MA:, mol %: 90-60; 10-40; t: 0-30°C; catalysis/MA: 0,1-1,0).

IR spectra data, cm^{-1} 2750, 1760, 1725, 1555 and 1410 (γ C=O); 1610, 900, 840, 730 and 705 (phenyl p.); 1635 (γ C=O); 2900-3150 (γ CH and CH_2).

Measurements and Analyses

The IR spectra of polymer films were recorded by use of (Py-Unicam Sp-1025) spectrophotometer.

Photosensitivity of thin polymer coatings formed on glass surface were determined by change of their optical densities in UV-irradiation. The Osram-Ultra Vitalax E 27 moderate pressure UV lamp (300 W) served as a source of irradiation.

Thermal analysis

Thermogravimetry (TGA) and different; al thermal analysis (DTA) experiments were carried out by use of a Paulik-Erday derivatograph system. The thermal stability of modified PS has been arbitrarily defined by initial loss observed with increase in temperature at 10 °C/min heating rate on the air atmosphere.

Differential Scanning Calorimeter analysis were realized by use of a Dupont TA 2000 at an under of 10 °C/min heating rate nitrogen atmosphere.

Physico-mechanic analysis

The adhesion capability, relative extension and resistance to stretch were determined by RMI-250 apparatus. In this measurement, the sample was determined by stretching.

Resistance to stretch (σ): It can be calculated as following:

$$\sigma = \frac{P}{a \times h} = \frac{P}{A}$$

where, P , the weight to which the sample is subjected, kgf; a , the width of sample, cm; and h , the thickness of sample, cm.

The relative extension (ϵ') (%): It can be calculated as using the equation:

$$\epsilon' = \frac{l - l_0}{l_0} \times 100$$

where, l_0 , the initial part of working sample, mm; and l , the breaking part of working sample, mm.

Adhesion capability (A): The adhesion capability is calculated by the using following equation:

$$A = \frac{P}{S}$$

where, A , adhesion (MPa); P , the force for stretch, kgf; and S , the exposed surface area sample, cm^2 .

$$S = a \times b$$

a , the width of signboard, cm; and b the exposed adhesion area, cm.

Resistance to stroke (α): It was determined by resistance to stroke using KM-15-1 apparatus. The resistance to stroke at the breaking time could be calculated (according to standard 120×15×10 mm) from the following equation:

$$\alpha = \frac{W}{a \times h}$$

where, W , the work for breaking the sample, kgf/cm.

Brinell Hardness (H_B): The hardness Brinell was determined by AS-101/KM-2 apparatus and was measured as (N/mm^2) according to standard.

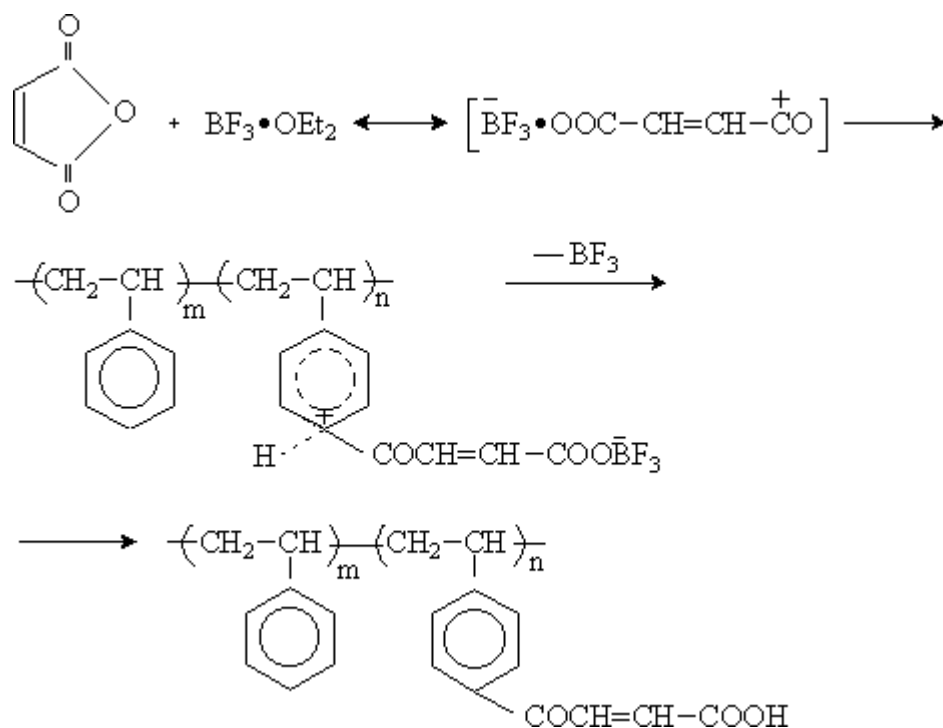
Resistance to heat (T_v): It was determined by FWA model Vika apparatus. The heat rate was 50 °C/h.

Results and Discussion

In our earlier paper, the some physico-chemical properties of the acylated reaction of PS with maleic anhydride by using of Lewis acid catalysts were

investigated in the presence of cationic catalysts [10,11].

The acylation reaction mechanism of the PS with MA in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ catalysts is as following:



Scheme 1

The mechanism of the acylation reaction of PS with acetic anhydride in the presence of Lewis catalysts can be considered as shown on Scheme 2.

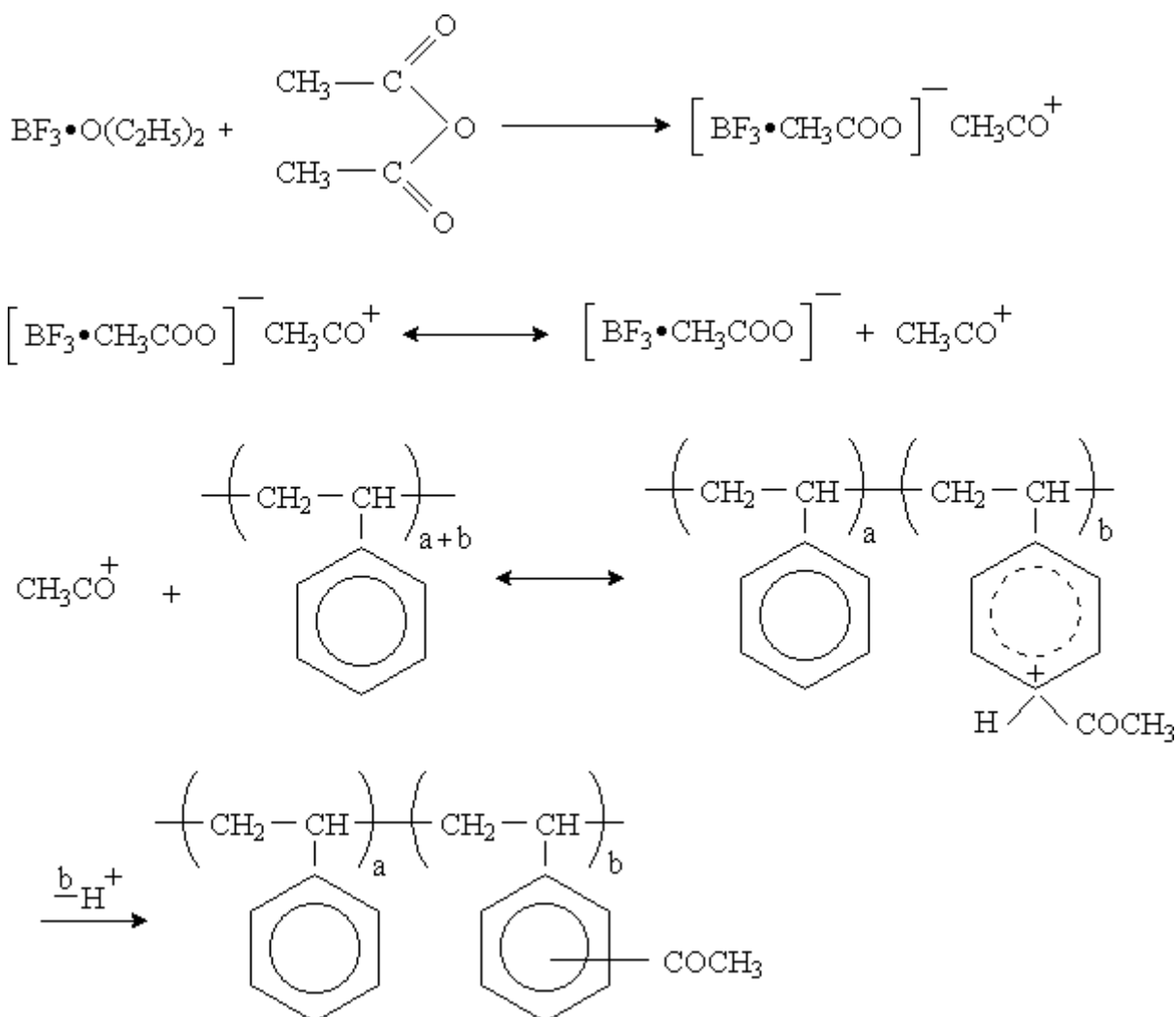
The anchoring of the CH_3-CO - group to the aromatic ring of PS was confirmed by spectral and chemical methods, for confirmation of the anchored CH_3-CO - group to the CH_3-CO - group was converted to the $(\text{CHCOH})-\text{CH}_3$ group by hydrogenation reaction with LiAlH_4 .

When compared of the bonding groups to the aromatic ring of PS between MA and AA as a mol%, the higher bonding was obtained with MA and this is found to be mine then that of AA. These results were also confirmed by determination of the kinetic parameters between MA and AA, under the same reaction conditions, and the obtained kinetic parameters are given in Table 1. As shown in Table 1, if the initial rate (W_0) and rate constant (K) of the acylation

reaction between MA and AA are compared, the MA is almost 10-14 times higher than AA in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ catalysts. This fact is due to the stretching structure of MA and the effect of the catalysts.

The physico-mechanical, thermal and adhesion properties of the synthesized polyfunctional PS's are dependent on the nature of functional ($\text{CH}_3\text{CO}-$; $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$) groups in the aromatic ring. The results of for physico-mechanic, thermal and adhesion capability properties of the synthesized polyfunctional PS's are given in Table 2.

The physico-mechanic, thermal and adhesion properties increased from 4.5 mol% to 20.0 mol%. when $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$ groups bonded to the aromatic ring of PS and the following changes, were obtained; the resistance to stroke of PS increased from 14.0 to 19.2 kJ/m². The resistance to stretch polymer material itself increase from 40.0 to 63.5 MPA, and



Scheme 2

Table 1

Kinetic Parameters of Acylation Reaction of PS with MA and AA in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ catalysts

T, K	$W_0 \times 10^5 \text{ mol/L} \times \text{s}$		$K \times 10^4 \text{ L/mol} \times \text{s}$		$E_a, \text{ kJ/mol}$	
	MA	AA	MA	AA	MA	AA
298	15,8	1,1	12,7	0,9		
323	21,6	2,1	17,1	1,6	11,3	17,1
343	28,3	3,1	22,7	2,3		

adhesion capability to metal surfaces increased from 2.2 to 7.3 MPA. Furthermore, the sensitivity of the polymer to light ($87 \text{ cm}^2/\text{J}$) was increased and the higher the thermostability (according to DTA and TGA analysis) was determined.

When the quantity of $-\text{CO}-\text{CH}_3$ bonding group to PS was increased from 4.4 mol% to 9.8 mol%, the

following changes were observed; the resistance to stretch was increased from 53.9 to 62.0 MPA and the adhesion capability was also increased from 0.5–2.4 MPA. As shown in Table 2, the adhesion capability was increased, on the contrary, and difference in the resistance to stretch for the carboxyl and acetyl groups was not observed. These observations demonstrate that

Table 2
Physico-mechanic, Thermal and Adhesion Properties of Functional Polystyrenes

Functional group	Mol %	σ (MPA)	α (KJ/m ²)	ϵ' (%)	T _v (°C)	H _B (N/mm ²)	A (MPA)	Mn×10 ⁻⁴
-CO-CH ₃	9.8	62.0	9.0	16.1	115	195	2.4	37.0
-CO-CH=CH-COOH	20.0	63.5	19.2	17.5	100	180	7.3	40.5
PS	-	35.0	13.0	1.5	80	180	0.2	50.0
After destruction of PS	-	30.0	10.5	2.1	76	125	0.5	30.0

(σ): resistance to stretch, (α): resistance to stroke, (ϵ'): relative extension, (T_v): resistance to heat, (H_B): hardness, (A): adhesion

the different functional (carboxyl-, keto, acetyl-) groups can be attached to the aromatic ring of PS with various chemical modification conditions, and it is possible to obtain different technical properties for polymer materials.

References

1. N.G. Gaylord, R. Mehta, V. Kumar and M. Taki., J. Appl. Polym. Sci., 38, 359 (1989)
2. N.G. Gaylord, R. Mehta, D.R. Mohan and V. Kumar., J. Appl. Polym. Sci., 44, 1941 (1992).
3. N. Mitsuaki and A. Masuasu, J. Chem. Soc. Jpn., 70, 1452 (1970)
4. C.-J. Wu, C.-V. Chen, E. Woo and J.F. Kuo, J. Polym. Sci. Polym. Chem., A, 31, 3405 (1993)
5. J. Ayres and C.K. Mann., J. Polym. Sci. Polym. Phys. B, 3, 505 (1965)
6. C.R. Harrison, P. Hodge, J. Kemp and G.M. Perry, Macromol. Chem., 176, 267 (1975)
7. R. Kurbanova, A. Ragimov and K. Aslanov, Zh. Prikl. Khim., 1, 2311 (1979)
8. R. Kurbanova, D. Aliyeva and A. Ragimov, J. Lakokras. Mater. 1, 51 (1980)
9. R. Kurbanova, A. Mehraliyev and T. Orucova, J. Lakokras. Mater. N 3, 34 (1981)
10. R. Kurbanova, R. Mirzaoglu, G. Akovali, Z.M. Rzayev, I. Karatas and A. Okudan, J. Appl. Polym. Sci., 59, 235 (1996)
11. R. Kurbanova, R. Mirzaoglu, S. Kurbanov, I. Karatas, V. Pamuk, E. Özcan, A. Okudan and E. Güler, J. Adhesion Sci. and Technol., Vol.11, N 1, 105 (1997)

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