

THE EFFECT OF SURFACE CARBON FUNCTIONAL GROUPS ON ACRYLONITRILE, STYRENE AND PINENES POLYMERIZATION

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Introduction

It has been reported that cationic and anionic polymerization of styrene and other cyclic monomers is initiated by an oxidized carbon black surface or by carbon fibers [1-5]. The introduction of functional groups such as phenolic or carboxyl onto a carbon surface has the ability to initiate polymerization reactions [1].

Pinene homopolymers belong to the family of terpenic resins that are low molecular weight valuable commercial products used by the adhesive, sealant, wax coating and casting industries. They are bicyclic isomers that undergo cationic polymerization by ring opening of its cyclobutane ring [6].

In this present study an oxidized activated carbon was used as catalyst for styrene, acrylonitrile, α - and β -pinene polymerizations.

Experimental

The surface of a commercial granular carbon (Norit, GCN, C0.0) was modified with several treatments, namely with different concentrations of HNO₃ (0.5M; 2.5M; 5M; 7M and 15M. The samples respectively, denoted C0.5, C2.5, C5, C7 and C15, were heated at 90°C during 6 hr. The sample C5 was treated at 25°C during 6 hr.

After treatments the samples were washed until neutral pH was achieved, and dried at 110°C before use. The sample denoted Cair was gasified in air at 350°C during 3 hr.

The surface of the as received and modified carbons were analysed by XPS using a XSAM800 (KRATOS) X-Ray Spectrometer operated in the FAT mode, with a passage energy of 20 eV and non monochromatised Mg X-radiation ($h\nu=1253.7\text{eV}$). All sample transfers were made in air. The curve fitting was carried out with a nonlinear least squares algorithm using a mixture of Gaussian and Lorentzian peak shape, for component peaks.

Table 1 reports the binding energy (BE) values adopted in C_{1s} and O_{1s} curve fittings.

All these carbon samples were used as catalysts in the polymerizations mentioned above.

All the homopolymerization reactions were carried out at 90°C during 50h, except for acrylonitrile that were conducted at 50°C. The reactions were performed with magnetic stirring in microvials (5 cm³) using 0.125g of carbon sample, 1.25 cm³ of toluene and 0.02mol of monomers (α -pinene, β -pinene, acrylonitrile and styrene). After 50h the reaction was stopped by addition of an excess of methanol, in order to precipitate the polymer.

The conversion was calculated by the following equation: conversion (%) = A/B x 100 (A- polymer precipitated (g) + polymer on carbon surface (g); B - charged monomer (g)).

The polypinenes are oligomers (yellow viscous oils) that were recovered under vacuum distillation. The polystyrene obtained was also a low molecular weight product.

Results and discussion

Table 2 shows the physical characteristics of the samples used. For oxidized samples no significant surface changes were observed (except for sample C15), in agreement with previous studies [7]. In contrast the value of PZC decreases as oxygen content increases.

Table 3 list the relevant peak areas in the C_{1s} and O_{1s} regions.

Due to the high electronegativity of oxygen, the O_{1s} signal is not very sensitive to the way in which the oxygen is bound. More information is gained from C_{1s} peak.

Oxidation with HNO₃ (0.5; 2.5; 5; 7M) slightly increases oxygen content. The sample C15 exhibit a higher content of oxygen and seems to be enriched with more carboxylic groups than the others referred above. For these samples, also nitrogen oxide was detected excepting for sample Cair.

Table 4 shows the results obtained for polymerization conversions at 90°C, in air using the modified carbons as catalysts.

For α - and β -pinene polymerizations the conversion seems to be independent of the surface treatments. In a previous work [6] the conversion obtained for a sample with low C-OH groups was very low suggesting that those weak acid centers promote α - and β -pinene polymerization.

In the case of styrene polymerization much higher conversions were obtained for samples enriched in carboxylic groups such C15 [5]. These behaviour suggest that stronger acidic centers promote cationic styrene polymerization.

No polymerization of acrylonitrile was observed under these experimental conditions.

Table 1. Binding energies of C_{1s} and O₁ XPS signals.

Carbon atom type		BF (eV)
C ₁	graphitic	284.3
C ₂	aliphatic	285.1
C ₃	alcoohls	286.8
C ₄	keto groups	288.0
C ₅	carboxylic groups	288.7
C ₆	carbonate, CO ₂	290.4
C ₇	plasmon	292.4
Oxygen atom type		
O ₁	aromatic C = O	530.8
O ₂	aliph. COC, C-OH, C=O, COOR/H	532.5
O ₃	phenol, COOR/H	533.8
O ₄	adsorbed H ₂ O	536.8

Table 2. Physical and chemical characteristics of the activated carbons.

Sample	S _{N2} (m ² /g)	%C	%O	%N	PZC
C0.0	929	93.7	5.8	0.5	7.6
C0.5	939	88.2	10.8	1.0	-
C2.5	794	86.2	12.8	1.0	-
C5	865	85.1	13.5	1.4	-
C7	867	83.1	15.7	1.2	3.3
C15	504	68.0	30.6	1.4	2.7
Cair	990	91.9	7.6	0.5	-

Table 3. Area (%) of the relevant peaks of activated carbons reported to 100% C_{1s} and 100% O_{1s}.

Samp	C ₃	C ₄	C ₅	O ₁	O ₂	O ₃
C0.0	13.5	2.5	0.3	21	49	16
C0.5	14.1	1.4	0.8	24	45	19
C2.5	14.8	1.7	0.3	22	51	16
C5	13.4	2.4	0.4	20	53	16
C7	14.7	1.9	0.4	21	51	17
C15	6.0	5.0	10	19	28	32
Cair	13.9	2.3	0.5	21	39	23

Table 4. Polymerization conversion using carbon as catalyst (T=90°C, t=50h, air).

Carbon	Conversion (%)		
	α -Pinene	β -Pinene	Styrene
C0.0	13	37	3
C0.5	18	26	2
C2.5	13	28	1
C5	10	27	1
C7	13	27	5
C15	15	20	45
Cair	13	35	9

Conclusions

- Styrene polymerization seems to be promoted by strong acidic centers such as carboxylic groups.
- The results obtained for α - and β -pinene oligomerizations suggest that weak acidic centers such as phenolic groups promote these reactions.

References

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