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SYNTHESIS OF FLUORINATED POLYSTYRENE

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Received: October 15, 2007

Abstract. Acylation of polystyrene with trifluoroacetic anhydride in a solution of aprotic solvents, namely 1,2-dichloroethane, chlorobenzene at the presence of Lewis acid as a catalyst results in obtaining fluorinated polystyrenes, which possess trifluoroacetic fragments in a benzoic ring, preferably in the position 4. In order to achieve 70 % substitution of benzene rings in polystyrene macromolecules, the ratio polystyrene: trifluoroacetic anhydride : AlCl_3 must be at least 1:2:4.4 mol correspondingly.

Keywords: modification, polystyrene, trifluoroacetic anhydride, fluoropolymers

1. Introduction

It is well known, that fluoropolymers are characterized by a complex of unique properties, such as high thermal and chemical stability, poor solubility in organic solvents, biocompatibility *etc.* [1, 2]. At the same time another point of a great practical importance is surface properties of fluoropolymers: poor adhesion, low friction coefficient, hydrophobicity, high scratch resistance *etc.* [3].

Today fluorinated analogues of all known classes of polymers are obtained and fluoropolymers are represented in a wide range. As usual, fluoropolymers are obtained by the polymerization or polycondensation reaction of appropriate fluoromonomers [4]. However they are quite expensive due to complicated production technologies. This factor is the main barrier on the way to wide implementation of fluoropolymers.

It was shown by Zisman [5], that perfluorinated organic compounds are characterized by very low surface energy. Perhaps the reason of this fact is a well-ordered construction of the surface layers, which contain $-\text{CF}_2-$ or $-\text{CF}_3$ fragments. In some specific cases such layers can form high ordered surface micro hetero phases [6, 7]. Due to their extremely low surface energies polymers with fluorocarbon segments in side chains have recently received particular attention [8-19].

On the other hand the surface properties of fluoropolymers can be reproduced by the method of introduction of perfluorinated fragments $-(\text{CF}_2)_n-\text{CF}_3$ into traditional polymers.

Today this approach is especially urgent because a long list of fluorinated organic compounds such as carbon acids, alcohols, amines *etc.* are industrial products. Attaching perfluorinated side chains to traditional polymers allows combining properties of the last ones with specific properties of micro hetero phases, formed by perfluorinated side fragments. This approach was confirmed by obtaining perfluorinated polyacrylates and polymethacrylates [20-22].

2. Experimental

2.1. Materials

Polystyrene (PS 148H, Germany), trifluoroacetic anhydride 99.5 % and AlCl_3 (both from Aldrich) were used without preliminary purification. Solvents (1,2-dichloroethane, chlorobenzene, dimethylformamide, ether) were purified in accordance with [23].

2.2. Synthesis of fluoropolystyrene

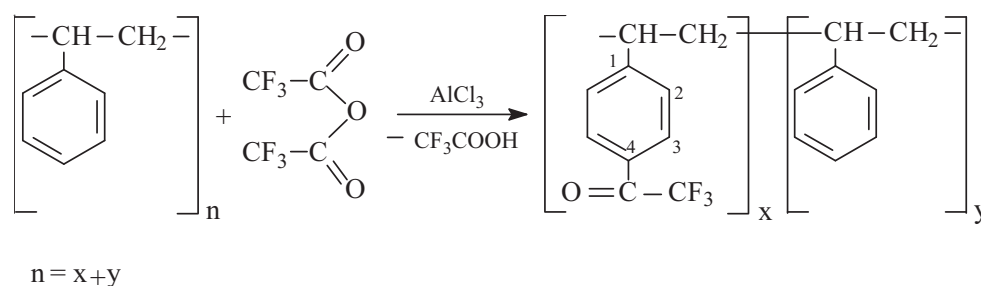
1.0 g (0.0096 mol) of polystyrene has been loaded to 150-200 ml three-neck flask, equipped with the stirrer, condenser, pipe for inert gas purging and thermometer. The condenser has a small catcher with CaCl_2 in his top part to prevent the water vapour penetration into the reactor. Polystyrene has been dissolved in 30 ml of dry 1,2-dichloroethane while heating, then cooled to 293 K and 4.0 g (0.0190 mol) of trifluoroacetic anhydride was added (2 mol per 1 mol of polystyrene). Under the flow of inert gas 2.53 g (0.0190 mol) of AlCl_3 was added by small batches during 10-15 min and the mixture was stirred during 1 h at 288-293 K and then 3 h at approx. 353 K. During this period the mixture becomes yellow and brown. The suspension is cooled to 293 K, 10 ml of dimethylformamide (DMFA) is added, then it is filtered through the filter paper and the precipitate is washed with 10 ml of 1,2-dichloroethane. 60-70 ml of ether is added to the filtrate in order to precipitate the modified polystyrene. After several hours in a refrigerator the liquid is amalgamated from the resin again. The resin is squashed with filter paper and dried primarily on air and then under

vacuum at 333–353 K. Approx 1.5 g of fluorinated polystyrene has been yielded as a solid brown substance.

The amount of trifluoroacetic anhydride can be varied from 1 to 4 mol per 1 mol of polystyrene and the amount of AlCl_3 is 0.5–4.0 mol per 1 mol of trifluoroacetic anhydride.

2.3. Methods of analysis

The content of fluor was determined by the method described in [24]. Infrared spectra (IR) were obtained using Specord M-80 apparatus, Carl Zeiss, Jena, Germany, with the relevant absorption interval in the 4000–400 cm^{-1} range and NMR spectra, using Bruker AC-F 300 M in $\text{CD}_3\text{-C(O)-CD}_3$ acetone. Hexamethyldisiloxane was used as the internal standard. Chemical shift of proton signals was determined by the positions of centers of symmetry.



This method allows to adjust the degree of substitution and as a result – the content of fluorinated fragments in modified polystyrenes. The presence of $\text{CF}_3\text{C(O)}$ groups was confirmed by IR and NMR-spectroscopy, element analysis and by determination of fluorine content. The general characteristics of the products obtained are shown in Table. The amount of AlCl_3 catalyst was equimolar to the TFA amount in all syntheses. The analysis of NMR spectra shows that trifluoroacetic groups enter preferably in *n*-position in relation to ethylene substitute. This fact can be explained by the steric hindrances which occur in *o*-positions.

Table

Characteristics of fluorinated polystyrenes

The molar ratio TFA:PSt	Solvent	Content of fluor, %	Degree of substitution, x/n
1:1	1,2-Dichloroethane	7.3	0.26
1:1	Chlorobenzene	6.6	0.23
1.36:1	1,2-Dichloroethane	8.4	0.29
2:1	1,2-Dichloroethane	11.4	0.40
4:1	1,2-Dichloroethane	18.6	0.65

Obtained fluorinated polystyrenes contain from 7.3 to 18.6 % of fluorine, depending on the molar ratio polystyrene : trifluoroacetic anhydride and insufficiently on the nature of the solvent. The acylation occurs a bit better in 1,2-dichloroethane, due to better solvation of intermediate ions. At the same time it can be seen from Table that no more than 25 % of initial amount of TFA reacts with polystyrene.

3. Results and Discussion

Polystyrene macromolecules consist of elementary links of phenyl ethylene, the benzoic rings of which are activated to electrophilic reagents action due to alkyl substitute with +I-effect. These rings tend to reactions of electrophilic substitution and can be slightly acylated under Friedel-Krafts conditions. This peculiar property of polystyrene was used for introduction of trifluoroacetic fragments into benzoic rings. Polystyrene was acylated by trifluoroacetic anhydride (TFA) in the media of aprotic anhydrous solvents (1,2-dichloroethane or chlorobenzene) in the presence of Lewis acid as a catalyst. The scheme of the process can be described as follows:

An interpretation of IR spectra of certain fluorinated polystyrenes shows that intensive stretching of carbonyl bonds in trifluoroacetic groups – $\nu(\text{C=O})$ – appears at 1664 cm^{-1} , $\nu(\text{C---F})$ stretches – at 1200 and 1152 cm^{-1} . The carbon-carbon bonds in a benzoic ring stretch at 1600, 1512, 1540 cm^{-1} and $\delta(\text{C---H})$ – at 1432, 1368 cm^{-1} .

In $^1\text{H-NMR}$ spectrum the protons of acylated rings appear in downfield at 7.58 (3) and 7.22 (2) ppm. Simultaneously, the signals of the protons in unsubstituted rings result at 7.10–7.13 ppm. Aliphatic protons create signals in upfield within the range 2.60–1.12 ppm. The shifts of aromatic protons signals in fluorinated polystyrenes to downfield testify the strong electron accepting properties of trifluoroacetyl fragments.

The dependence of the degree of substitution (D.S.) on the molar ratio trifluoroacetic anhydride–polystyrenes is shown in Fig.1.

One can see from Fig. 1 that correlation of D.S. with the amount of TFA has the linear character, at the same time the efficiency of its usage is not high. In order to achieve the total acylation in the benzene rings, the ratio of TFA to polystyrene units should be approx. 10 to 1.

With regard to the catalyst, its amount affects the degree of substitution too. The dependence of the degree of substitution on the amount of AlCl_3 catalyst is shown in Fig.2.

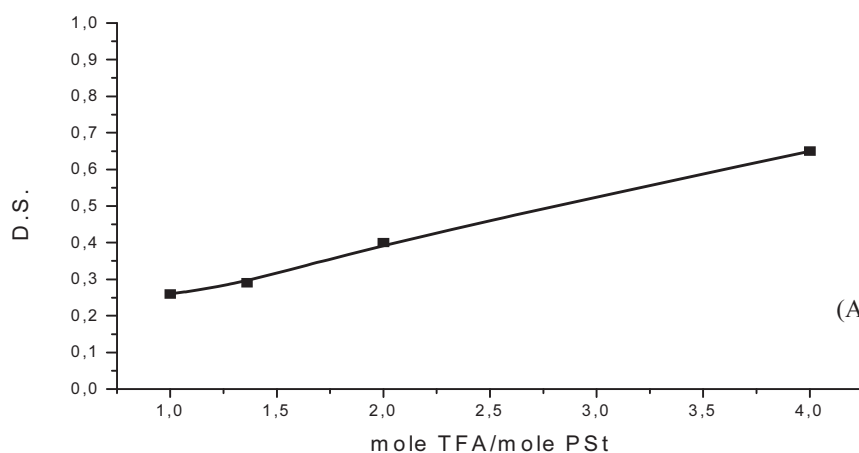


Fig. 1. Dependence of the degree of substitution (D.S.) on the molar ratio trifluoroacetic anhydride–polystyrene. (Amount of AlCl_3 is 1.5 mol per mol of TFA)

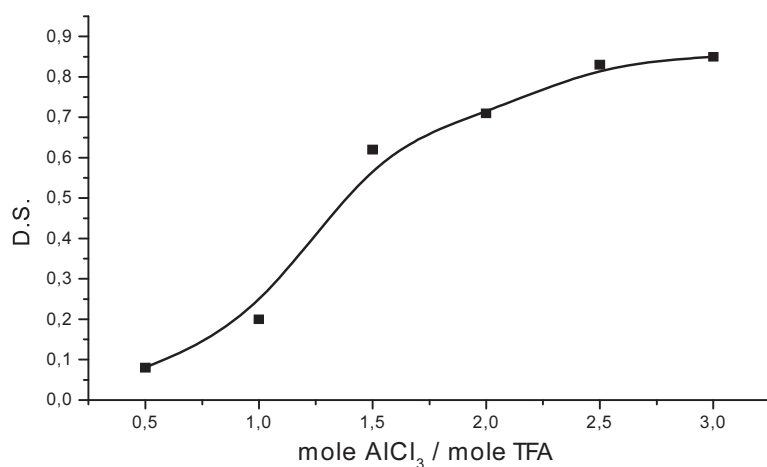
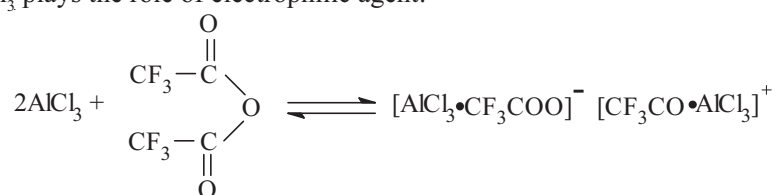


Fig. 2. Dependence of the degree of substitution on the molar ratio catalyst: trifluoroacetic anhydride. (The ratio PSt:TFA = 1:2)

One can see from Fig. 2 that D.S. grows if the amount of the catalyst in the reaction mixture is increased. But if its amount reaches 2 moles, this increasing becomes inessential.

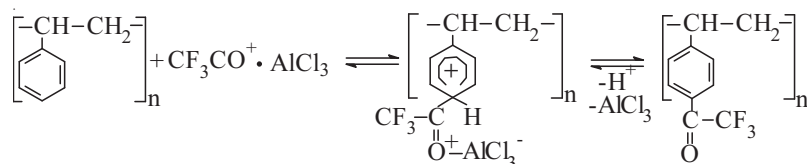
Such a correlation becomes clear considering the mechanism of the process. Acylation reaction is a typical electrophilic displacement in the benzoic rings of the polystyrene, in which solvated ion trifluoroacetylum (CF_3CO^+) or its complex with AlCl_3 plays the role of electrophilic agent:



In accordance with this scheme the formation of one mole of electrophile (CF_3CO^+) needs 2 mol of AlCl_3 per 1 mol of TFA [25]. Furthermore some amount of the catalyst undergoes deactivation due to the interaction with trifluoroacetic acid, which is the by-product of the acylation reaction:



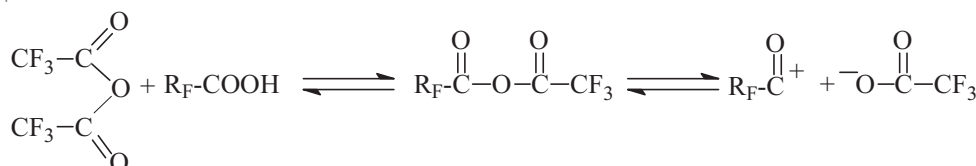
The electrophile formed attacks the benzoic ring of polystyrene macromolecule forming at first the σ -complex and then poly(4-trifluoroacetylstyrene):



It is important to highlight that if the degree of substitution increases the solubility of the polymer in chlorobenzene and dichloroethane goes down. Fluorinated polystyrenes with the degree of substitution more than 0.6 are practically insoluble in dichloroethane. They can be soluble only in dimethylformamide. This fact is very important if fluorinated polystyrenes would be used for preparation of polymeric compositions. A poor solubility in components of composition throws out fluorinated

polystyrene onto the surface and makes its properties the same as fluoropolymers have.

Moreover, trifluoroacetic anhydride could be used as the catalyst for acylation reaction of polystyrene by another aliphatic fluorinated acid. As a result of the interaction of trifluoroacetic anhydride with organic acid the hybrid anhydride is formed, which is able to form electrophile from that part of its molecule, which does not belong to trifluoroacetic fragment [26]:



As a result the acylic fragments of other fluorinated acids could be introduced into polystyrene.

4. Conclusions

1. Trifluoroacetic fragments can be introduced into the aromatic ring of polystyrene by acylation reaction of polystyrene with trifluoroacetic anhydride at 353 K in the media of chlorinated aprotic solvents.

2. The degree of substitution has a linear correlation with the ratio trifluoroacetic anhydride : polystyrene.

3. In order to achieve a 70 % substitution of the benzene ring in polystyrene units the molar ratio polystyrene : trifluoroacetic anhydride : AlCl_3 must be 1:2:4.4 moles correspondently.

References

- [1] Akemi H., Aoyagi T., Shinohara I., Okano T., Kataoka K. and Sakurai Y.: *Macromol. Chem.*, 1986, **187**, 1627.
- [2] Kambic H., Murabayashi S. and Nose Y.: *Chem. Eng. News*, 1986, **64** (15), 30.
- [3] Schmidt D., Coburn C., DeKoven B., Potter G., Meyers G. and Fischer D.: *Nature*, 1994, **368**, 39.
- [4] Pittman A. and Wall L.: *Fluoropolymers*. Wiley-Interscience, New York 1971.
- [5] Zisman W.: *Contact Angle, Wettability, and Adhesion*. Advances in Chemistry Series 43. American Chemical Society, Washington, DC 1964.
- [6] Schneider J., Erdelen C., Ringsdorf H. and Rabolt J.: *Macromolecules*, 1989, **22**, 3475.
- [7] Torstensson M., Ranby B. and Hult A.: *Macromolecules*, 1990, **23**, 126.
- [9] Fox H. and Zisman W.: *J. Colloid Sci.*, 1950, **5**, 514.
- [8] Bernett M. and Zisman W.: *J. Phys. Chem.*, 1962, **66**, 1207.
- [10] Roitman J. and Pittman A.: *Polym. Lett.*, 1972, **10**, 499.
- [11] Pittman A. and Ludwig B.: *J. Polym. Sci. A1*, 1969, **7**, 3053.
- [12] Pittman A., Sharp D. and Ludwig B.: *J. Polym. Sci. A1*, 1968, **6**, 1729.

- [13] Ramharack R. and Nguyen T.: *J. Polym. Sci. C, Polym. Lett.*, 1987, **25**, 93.
- [14] Yokota K. and Hirabayashi T.: *Polym. J.*, 1985, **17**, 991.
- [15] Lin J., Dudek L. and Majumdar D.: *J. Appl. Polym. Sci.*, 1987, **33**, 657.
- [16] Park I., Lee S. and Choi C.: *J. Appl. Polym. Sci.*, 1994, **54**, 1449.
- [17] Chapman T., Benrashed R., Marra K. and Keener J.: *Macromolecules*, 1995, **28**, 331.
- [18] Guerry-Rubio C., Viguier M. and Commeyras A.: *Macromol. Chem. Phys.*, 1995, **196** (4), 1063.
- [19] Beyou E., Bennetau B., Dunogues J., Babin P., Teyssie D., Boileau S. and Corpard J.: *Polym. Int.*, 1995, **38**, 237.
- [20] Guyot B., Ameduri B., Boutevin B., Melas M., Viguier M. and Collet. A.: *Macromol. Chem. Phys.*, 1998, **199**, 1879.
- [21] Ameduri B., Bongiovanni R., Malucelli G., Pollicino A. and Priola A.: *J. Polym. Sci. A*, 1999, **37**, 77.
- [22] Corpard J.-M., Girault S. and Juhue D.: *Langmuir*, 2001, **17**, 7237.
- [23] Weissberger A. and Proskauer E.: *Organic Solvents*. Interscience Publishers, Inc., New York 1955.
- [24] Hudlicky M.: *Chemistry of Organic Fluorine Compounds*. 2nd edn., John Wiley & Sons, 1976.
- [25] Norman R. and Taylor R.: *Electrophilic Substitution in Benzenoid Compounds*. Elsevier Publishing, New York 1965.
- [26] Cope A.: *Organic syntheses. An annual publication of satisfactory methods for the preparation of organic chemicals*. John Wiley & Sons, New York 1950.

СИНТЕЗ ФЛУОРОВАНОВОГО ПОЛІСТИРЕНУ

Анотація. Ацилюванням полістирену трифлуорооцтовим ангідридом у розчині апротонних розчинників (1,2-дихлоретану, хлоробензену) в присутності кислоти Льюїса як каталізатора були одержані флуоровані полістирени з трифлуорооцтовими фрагментами в бензольному кільці, переважно в положенні 4. Для досягнення 70 % заміщення в бензеновому кільці макромолекул полістирену необхідно, щоб співвідношення полістирен:трифлуорооцтовий ангідрид: AlCl_3 було відповідно 1:2:4.4 моль.

Ключові слова: модифікація, полістирен, трифлуорооцтовий ангідрид, флуорополімери