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AN EFFICIENT DEHYDROFLUORINATING SYSTEM FOR POLYVINYLIDENE FLUORIDE

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Chemical dehydrohalogenation of halogen-containing polymers is an accessible and convenient method for preparation of carbon-chain polymers with a system of conjugated multiple bonds in the main chain, including carbyne [1]. The development of an efficient method of preparation of carbyne and articles made of it is still an urgent problem. It was previously shown that chemical dehydrohalogenation of polyvinylidene halides (PVDH) with an alcohol solution of a base causes the formation of a cumulene modification of carbyne [2]:

$$-(-CH_2-CX_2-)_n \xrightarrow{-2nHX} = (=C=C=)_n$$
, where $X = F$. Cl. Br.

In the PVDH series, polyvinylidene fluoride (PVDF) is the most promising starting polymer for fabricating carbyne articles due to its better solubility. However, dehydrofluorination of PVDF takes place slowly due to the highest strength of the halogen-carbon bond in the order C-F > C-Cl > C-Br [3]. Addition of several polar solvents (DMSO, pyridine) to an alcohol solution of a base significantly accelerates the dehydrohalogenation reaction [1]. An efficient system, a mixture of a solution of KOH in ethanol with tetrahydrofuran (THF), was used in [2] for dehydrohalogenation of PVDH. The use of THF allowed conducting the dehydrohalogenation reaction relatively efficiently in soft conditions – at room temperature and even lower. However, in this case, too, dehydrofluorination of PVDH took place slowly: the degree of dehydrofluorination of the films was only 70% after 28 h.



Fig. 1. Photoelectron spectra (ESCA) of the starting PVDF film (dashed line) and a film dehydrofluorinated for 1 h at 20°C (solid line).

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In searching for a more efficient dehydrofluorinating system, we found that a mixture of a solution (20 wt. %) of KOH in EtOH with acetone in a 1:9 volume ratio is a very efficient dehydrofluorinating system for PVDF. A film (20 μ m) treated with this mixture for 1 h at ~20°C had a carbyne structure and contained no more than 1 wt. % residual fluorine for the entire bulk (Fig. 1). It should be noted that this mixture was not very efficient with polyvinylidene chloride. This behavior can probably be explained from the point of view of the ratio of the surface energies of the halogen-containing polymer and reaction mixture. Since the starting polymers have different solubility parameters, by selecting the corresponding solvents and concentrations, it is possible to vary the ratio of the surface energies of the polymer and reacting medium and attain a more efficient reaction.

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