# Reduction of Poly(tetrafluoroethylene) by Aromatic Radical Anions: An ESR and NMR Study

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ABSTRACT: An ESR and <sup>19</sup>F-NMR study was carried out to elucidate the reduction kinetics of PTFE with aromatic radical anions (anthracene, benzophenone, biphenyl, and naphthalene), whose counter cation is Na<sup>+</sup>, in THF solvent. The ESR signal intensities of aromatic radical anions decayed according to the second-order equation whose rate depends on the kind of radical anions; the relative order being naphthalene  $(1.00) \ge$  biphenyl (0.03) > anthracene (0.02) > benzophenone (0.003). The defluorination from PTFE was examined by a high-resolution <sup>19</sup>F-NMR method of NaF disolved in an ethanol/water mixed solvent. When an excess amount of Na metal was present, the yield of NaF exceeded the initial concentration of aromatics. The result suggests that the aromatic radical anions are regenerated by the reaction with excess Na metal. The amounts of NaF salts produced during the reducing process were also followed by the same order as the decaying rates of aromatic radical anions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 286–289, 1999

**Key words:** reduction kinetics; aromatic radical anion; poly(tetrafluoroethylene); ESR; <sup>19</sup>F-NMR

## **INTRODUCTION**

The surface modification of poly(tetrafluoroethylene) (PTFE) has attracted much attention for wide usage of PTFE in medical, chemical, and electrical fields.<sup>1–11</sup> Various methods have been proposed so far for the surface modification. They include chemical modification.<sup>1–7</sup> electrochemical modification,<sup>8,9</sup> and physical modification using  $\gamma$ -rays<sup>10</sup> and plasma.<sup>11.12</sup>

Among them, the chemical modification of PTFE using aromatic radical anions is one of the most promising methods from a practical point of view because of a rather simple and economic method. The aromatic radical anions in organic solvent have been reported to reduce PTFE<sup>3</sup> as well as perfluoroalkane<sup>13</sup> and 1,2,3,4-tetrafluorobenzene.<sup>14</sup> For example, McCarthy et al.<sup>4</sup> have examined the reduction mechanism of PTFE with benzoin dianion in Me<sub>2</sub>SO<sub>4</sub> solvent by FT-IR and Raman spectroscopic methods. Nelson et al.<sup>3</sup> have studied the reduction of PTFE with naphthalene radical anion in THF solvent, and reported that the electron transfer from anion radicals to PTFE gives rise to the formation of a carbonaceous layer formed by defluorination of PTFE. However, little is known about the reduction kinetics of PTFE from which defluorination reaction occurs. In this article, the reduction of PTFE by aromatic radical anions (anthracene, benzophenone, biphenyl, and naphthalene) with Na<sup>+</sup> as a counter cation was studied by both electron spin resonance (ESR) and <sup>19</sup>F-NMR methods. The reaction rates were followed by observing the ESR spectral intensity

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**Figure 1** Schematic view of the sample tube used for ESR study.

of the radical anions in THF solution as a function of time at a constant temperature. Yield of NaF salt formed during the reducing reaction was determined by <sup>19</sup>F-NMR, which enabled examination of the degree of defluorination from PTFE.

### EXPERIMENTAL

The PTFE powder sample was supplied from Daikin Co., Ltd. The aromatic compounds such as anthracene, benzophenone, biphenyl, and naphthalene (Katayama), THF (Wako), and Na metal (Katayama) were used as received.

PTFE was reduced by the following two methods. (1) The aromatic radical anion was generated in the Spectrosil ESR sample tube illustrated in Figure 1 by contacting Na metal  $(1.3 \times 10^{-2} \text{ mol})$ with the aromatic compound  $(2.0 \times 10^{-4} \text{ mol})$ predissolved in THF (2.0 cm<sup>3</sup>) solvent at position (a). The reduction of PTFE (0.5–1.5 g; CF<sub>2</sub> unit:  $1-3 \times 10^{-2}$  mol) was initiated at 293 K by transferring the solution containing aromatic radical anions into the attached tube (b). After a certain

reaction time,  $1 \times 10^{-4} \text{ dm}^3$  of the solution was transferred into the main tube (c), and then ESR spectrum was recorded with JEOL JES-RE1X ESR spectrometer at 77 K. Hereafter, this is called Method I. (2) The second method (Method II) was performed according to the previous report.<sup>5</sup> A  $1.0 \times 10^{-3}$  mol of aromatics and a 2.2  $imes 10^{-2}$  mol of Na metal were dissolved into a 1 imes 10<sup>-2</sup> dm<sup>3</sup> of THF solvent at the same temperature under an Ar atmosphere to generate the associated aromatic radical anions. Then, PTFE was immersed into the THF solution at 293 K. The reduced PTFE was washed repeatedly with the mixed solvent of water and ethanol with 1:1 volume ratio, so as to completely remove both aromatics and NaF salt, the latter being a reaction product of  $Na^+$  with the fluoride anion  $(F^-)$ eliminated from PTFE.<sup>6</sup> After being dried for 24 h in vacuum, the PTFE sample was subjected to FT-IR and XPS measurements with a Perkin-Elmer SPECTRUM 2000 spectrometer and a Perkin-Elmer Electronics 5100 spectrometer using MgK $\alpha$  excitation (400 W, 15.0 KV), respectively. The NaF formed on PTFE surface was measured by the XPS method before washing the reduced PTFE. Furthermore, the NaF dissolved in the mixed solvent was measured by the <sup>19</sup>F-NMR method with a Bruker AMX 400 spectrometer; 1,2-Dibromo-1,1,2,2-tetrafluoroethane was employed as an internal standard of the <sup>19</sup>F chemical shifts.

## **RESULTS AND DISCUSSION**

We start with showing the ESR results on reduction kinetics using the sample prepared with Method I. When the THF solution with naphthalene was contacted with Na metal at 293 K for a couple of hours, the ESR spectrum due to naphthalene radical anion<sup>15,16</sup> was clearly observed. It was confirmed from the double integration of the ESR spectrum that all naphthalene molecules in THF were converted into the radical anions. Furthermore, the naphthalene radical anion was stable at 293 K, and no appreciable decaying was observed at least for 360 min at the same temperature.

During the reduction of PTFE, the ESR intensity of the naphthalene radical anion gradually decreased without any changes in line shape. The original white color of the PTFE surface first turned yellow to some extent, then gradually changed into gray. These strongly suggest that



**Figure 2** Testing plots of the aromatic radical anion concentration against the reaction time (Method I) by (a) first-order rate reaction, and (b) second-order rate reaction; naphthalene ( $\bigcirc$ ), biphenyl ( $\square$ ) anthracene ( $\spadesuit$ ), and benzophenone ( $\triangle$ ). The experimental error at the vertical axis was (1 (mol dm<sup>-3</sup>)<sup>-1</sup>.

naphthalene radical anion reacted with PTFE; the defluorination from PTFE is the most probable reaction responsible for it.<sup>5</sup> In fact, FT-IR spectra of the PTFE reacting with the naphthalene radical anion showed a new band at 1710  $\text{cm}^{-1}$  due to the monofluorinated olefin in addition to the characteristic bands of PTFE; 503, 640–620, 1150, and 1240  $\text{cm}^{-1.4}$ 

In order to get information on the reaction kinetics of naphthalene radical anion after contacting with PTFE, we tested to plot the radical anion concentration observed by ESR against the reaction time assuming the first-order (1) and secondorder (2) rate equation in Figures 2(a) and 2(b), respectively:

$$\ln[C] = \ln[C_0] - k_1 t$$
 (1)

$$[C]^{-1} = [C_0]^{-1} + k_2 t \tag{2}$$

where  $[C_0]$  and [C] stand for the radical anion concentration at reaction time t = 0 and t = t (min) respectively, and  $k_1$  (s<sup>-1</sup>) and  $k_2$  (mol<sup>-1</sup>s<sup>-1</sup>) are the associated rate constants. A linear correlation was obtained in Figure 2(b), but not in Figure 2(a), indicating that naphthalene radical anions decayed according to the second-order rate equation. Similar linear second-order plottings were obtained when the radical anions of anthracene, benzophenone, and biphenyl were used as a reducing regent instead of the naphthalene radical anion, but with different rate constants [see Fig. 2(b)]. It was found that the decaying rate of the naphthalene radical anion was independent of the concentration (number) of CF<sub>2</sub> in the range between 0.5 g PTFE (CF<sub>2</sub> unit:  $1 \times 10^{-2}$  mol) and 1.5 g PTFE (CF<sub>2</sub> unit:  $3 \times 10^{-2}$  mol): the number of fluoride atoms is much higher than that of the anion radical ( $2.0 \times 10^{-4}$  mol). From the slopes of the second-order plottings, the associated rate constants (relative values) were evaluated. Their order was naphthalene (1.00) >> biphenyl (0.03)> anthracene (0.02) > benzophenone (0.003). Note that a similar order has been reported for the reaction rate of  $n-C_8F_{16}$  with the aromatic radical anions.<sup>14</sup>

The above result suggests that two naphthalene radical anions reacted simultaneously with PTFE. McCarthy and his collaborators<sup>4</sup> have studied the reduction of PTFE with benzoin dianion in Me<sub>2</sub>SO<sub>4</sub> solvent and proposed reaction (3) shown in the scheme below. Here,  $\Phi$  stands for a phenyl group, whereas, Chakrabarti et al. reported that the reduction of PTFE with lithium in liquid ammonia solution resulted in the formation of the high-density polyethylene and proposed the following reaction (4) as a part of the mechanism for the reduction sequence.<sup>1</sup>



Although they have pointed out that the reduction of PTFE by anions might proceed according to the two-electron transfer reaction, no clear experimental evidence was provided for the reaction kinetics. The present result may be consistent with their earlier proposed reactions.

Here we move on the reducing reaction of PTFE under the presence of the excess Na metal (Method II). Fluoride anion  $(F^-)$  eliminated from



**Figure 3** The amount of NaF produced (Method II) was plotted against the reaction time; naphthalene ( $\bigcirc$ ), biphenyl ( $\square$ ), anthracene ( $\bullet$ ), and benzophenone ( $\triangle$ ). The reaction temperature was 293 K. The initial amount of aromatics was 1.0 × 10<sup>-3</sup> mol (corresponding to the dotted lines). The experimental error at the vertical axis was  $\pm 0.2 \times 10^{-3}$  mol.

PTFE is expected to react with Na<sup>+</sup>, a counter cation of aromatic anion, to yield NaF salt during the reducing reaction.<sup>6</sup> In fact, we could observe NaF formed on PTFE surface by XPS method. The NaF salt was, then, completely removed from the PTFE surface by repeatedly rinsing the sample with an ethanol/water mixed solvent. Thus, obtained mixed solvent with NaF gave its highresolution <sup>19</sup>F-NMR spectrum, which enabled us to evaluate the number of eliminated fluoride anions. Figure 3 shows how the amount of NaF increased with the reaction. For all the aromatic anion systems, the amount of NaF increased gradually with the reaction time and exceeded the initial amount of aromatics  $(1.0 \times 10^{-3} \text{ mol})$  except for the benzophenone system. The result indicates that radical anions were regenerated by the reaction with excess Na metal (see the reaction scheme in Fig. 3). The amounts of NaF salts produced during the reaction time from 10 to 240 min at 293 K were followed by the same order as the ESR results for the samples prepared by Method I; naphthalene  $\gg$  biphenyl > anthracene > benzophenone. The reason why such order was observed for the reaction rates is not yet clearly understood, but we could just note that the electron affinity of the aromatics may play an important role for the reaction rate. In fact, our cyclic voltammetry (CV) experiments resulted in that the one-electron reduction potential of the aromatic compounds fell in the same order; naphthalene, biphenyl > (-3.50 V) > anthracene (-3.30 V)V > benzophenone (-3.10V).

FT-IR spectra of reduced PTFE treated by Method II showed the bands around 2880, 2151, 1710, and 1626 cm<sup>-1</sup> due to the sp<sup>3</sup> type C—H stretching, C=C stretching, and C=C stretching of monofluorinated and nonfluorinated olefin respectively,<sup>1,4,6</sup> and the band from 1600 to 1400  $\text{cm}^{-1}$ attributable to skeletal vibrations of condensed aromatic-like carbon in addition to the characteristic bands of PTFE. The formation rate of each product, however, could not be evaluated correctly by the FT-IR because the formation reactions of each product are complex. However, the order of the amounts of NaF salts formed appeared to be in agreement with that of decaying rates of aromatic radical anions derived from ESR results, as mentioned above. The results suggest that overall reaction rates of PTFE with the anion radicals may be somewhat related to the decreasing rate of anion radicals according to the second-order equation, although further studies are required.

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