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Communications to the Editor

Mechanoions Produced by Mechanical Fracture of Solid Polymer. 6. A Generation Mechanism of Triboelectricity Due to the Reaction of Mechanoradicals with Mechanoanions on the Friction Surface

Many workers have tried to explain triboelectricity between insulators on the basis of modified band models.[1] However, no model is yet sufficient to explain triboelectricity completely. These band models do not identify specific molecular structures. From band models, it is hard to speculate on the signs of the charge induced by the friction.

Here we deal with triboelectricity as a phenomenon involving mechanical fracture of a polymer main chain on the friction surface. We will report a novel charge generation mechanism for the reaction of mechanoanions[2-6] and mechanoradicals[7-15] that are produced by the mechanical fracture of a polymer main chain.

Experimental Procedures. The solid polymers poly(methyl methacrylate) (PMMA; Aldrich Chemical Co., Ltd.), isotactic polypropylene (PP; Mitsubishi Petorochemical Co., Ltd.), polyethylene (PE; Sholex 6009, Showa Electric Industry Co., Ltd.), and poly(vinylidene fluoride) (PVDF; Kynar 720) and the electron scavenger tetracyanoethylene (TCNE; Katayama Chemical Co.) were purified as reported elsewhere.[2-6] Poly(tetrafluoroethylene) (PTFE: Aflon G80, Asahi Glass Co., Ltd.) was used without further purification. Each polymer was mechanically fractured in the presence of TCNE powder by a homemade vibration ballmill[7] in vacuo in the dark at 77 K for 21 h. Photoirradiation of the samples was carried out at 77 K with filtered infrared light (Metro WRH 125 IR lamp, Toshiba IRP70, IRD1A, R69, R60, Y50, and L39 glass filters). All samples were observed in vacuo in the dark at 77 K with 100-kHz field modulation by an X-band JEOL JES-ME electron spin resonance (ESR) spectrometer coupled to a Melcom 70 minicomputer (Mitsubishi Electric Co., Ltd.). ESR spectra were observed at a microwave power level of 2 μW to avoid power saturation. 1,1-Diphenyl-2-picrylhydrazyl was used to calibrate the magnetic field position on the ESR spectra.

Results and Discussion. ESR spectra from all polymers fractured with TCNE indicated that mechanoradicals were produced by homolytic scission of a carbon–carbon bond[7-15] in the main chain of the polymer, and TCNE anion radicals, $\text{TCNE}^{\bullet-}$, were formed by an electron subtraction reaction from the mechanoanions that were produced by heterolytic scission of a carbon–carbon bond.[2-5] It was reported[16] that the mechanoradicals were trapped on the fresh surface produced by fracture of the polymer. The ESR spectra of $\text{TCNE}^{\bullet-}$ indicate that electrons were transferred from the mechanoanions to TCNE by contact in the solid state. The following reaction process under milling in the dark for all polymers is suggested:

Homolytic scission of a carbon–carbon bond[7-15]

$$\underset{\text{polymer A}}{\text{A–A}} \rightarrow 2\text{A}^{\bullet} \tag{1}$$

Heterolytic scission of a carbon–carbon bond[2-6]

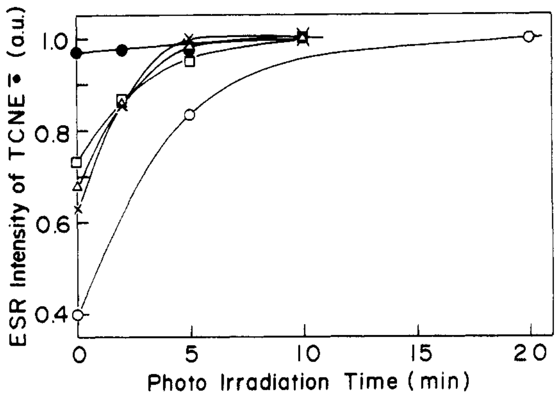

Figure 1. Relative ESR intensity of $\text{TCNE}^{\bullet-}$ in PMMA (●), PP (□), PE (△), PVDF (×), and PTFE (○) plotted against the photoirradiation time.

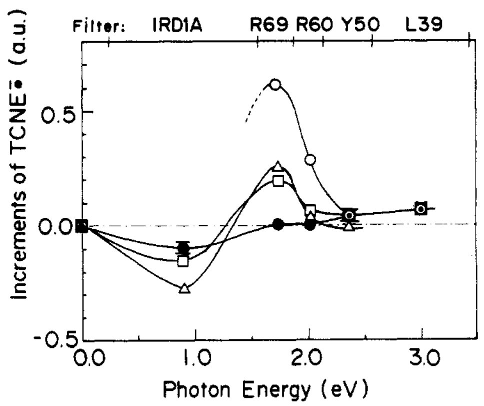

Figure 2. Increments of $\text{TCNE}^{\bullet-}$ in PTFE (○), PP (□), PE (△), and PMMA (●) plotted against the effective photon energy.

$$\text{A–A} \rightarrow \text{A}^{-} + \text{A}^{+} \tag{2}$$

Electron transfer due to contact in the dark[2-5]

$$\text{A}^{-} + \text{TCNE} \rightarrow \text{A}^{\bullet} + \text{TCNE}^{\bullet-} \tag{3}$$

where $\text{A}^{\bullet}$, A^{-}, and A^{+} are a mechanoradical,[7-15] a mechanoanion,[2-5] and a mechanocation[6] of polymer A, respectively.

After milling, all fractured samples were photoirradiated at 77 K by an infrared lamp with one glass filter (Toshiba IRP 70; 1.24 < photon energy range (PHOE) < 3.10 eV). The ESR intensity of $\text{TCNE}^{\bullet-}$ obtained from the peak height in a similar manner[2-5] increased with photoirradiation time and reached the plateau value shown in Figure 1, in which the intensity of $\text{TCNE}^{\bullet-}$ was normalized to the plateau value at 10-min photoirradiation for PMMA, PP, PE, and PVDF and at 20-min photoirradiation for PTFE. Almost no increase of $\text{TCNE}^{\bullet-}$ was observed from PMMA fractured with TCNE. This result means that almost all of the mechanoanions of PMMA were converted to $\text{TCNE}^{\bullet-}$ due to the reaction with TCNE under milling. The yields of $\text{TCNE}^{\bullet-}$ in reaction 3, i.e., under milling, were obtained from the intensity of the photoirradiation time for 0 min (summarized in Table I). The highest yield was obtained from PMMA fractured

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Table I
Yields of $TCNE^{\bullet-}$ in Polymers Fractured with TCNE by Milling in the Dark at 77 K

polymer	molecular structure	yield of $TCNE^{\bullet-}$ under milling, %	reactivity of A^-
PMMA	$-(CH_2C(CH_3)(COOCH_3))_n-$	97	high
PP	$-(CH_2CH(CH_3))_n-$	73	↑
PE	$-(CH_2CH_2)_n-$	68	
PVDF	$-(CH_2CF_2)_n-$	63	
PTFE	$-(CF_2CF_2)_n-$	40	low

with TCNE. The lowest yield was from PTFE fractured with TCNE. Table I shows that the reactivity of A^- with TCNE varied as follows from high reactivity to low: PMMA > PP > PE > PVDF > PTFE.

After milling, photoirradiations of a fractured sample for 10 min each at 77 K were carried out with glass filters (Toshiba IRD1A, 0.26 < PHOE < 1.57 eV; R69, PHOE < 1.88 eV; R60, PHOE < 2.14 eV; Y50, PHOE < 2.58 eV; L39, PHOE < 3.44 eV), which were used sequentially from the IRD1A to the L39 glass filter. The effective photon energy ranges were 0.26–1.57, 1.57–1.88, 1.88–2.14, 2.14–2.58, and 2.58–3.44 eV, based on the lamp wavelength output and the filter absorbance. The increments of $TCNE^{\bullet-}$ due to the photoirradiation are plotted against the effective photon energy range (Figure 2). Figure 2 shows that the most effective energy range for the increase of $TCNE^{\bullet-}$ is 1.57–1.88 eV. Since TCNE cannot migrate to the location of A^- at 77 K, the increase of $TCNE^{\bullet-}$ is due to the migration of an electron released from A^-, which is an unobservable chemical species by ESR spectroscopy, to TCNE to form $TCNE^{\bullet-}$, which is observable by ESR spectroscopy, in a manner similar to that reported elsewhere.[2-5] The increase of $TCNE^{\bullet-}$ means that the charge carrier is an electron, A^- is an electron donor, and TCNE is an electron acceptor.

The electron-release reaction of A^- is suggested:

$$A^- \rightarrow A^\bullet + e^- \qquad (4)$$

The most effective energy for the release of an electron from A^- in reaction 4 is called the electron-release potential of A^-, $Pr(A^-)$, in this article. This low $Pr(A^-)$ in a polymer, 1.57–1.88 eV, is supported by the ESR spectra of $TCNE^{\bullet-}$ from polymers fractured with TCNE powder in the dark at 77 K. Because the A^- were contacted with TCNE powder by mixing under milling in the dark at 77 K, the A^- released an electron due to the high molecular electron affinity of TCNE, Ea(TCNE), (=2.88 eV),[17] to produce $A^\bullet$ and $TCNE^{\bullet-}$ as already reported elsewhere.[2-5]

The intensities of both $TCNE^{\bullet-}$ and the total ESR spectra from PMMA, PP, and PE fractured with TCNE were decreased by photoirradiation with the IRD1A filter. No chain scissions, no anions, and no radicals were observed from photoirradiation with all the filters of unfractured polymer. The decrease of $TCNE^{\bullet-}$ and the total intensity seem to be a radical decay due to the molecular motion of the polymer induced by photoirradiation.

The $Pr(A^-)$ value in each polymer could not be estimated by the sequential photoirradiation experiments with five different filters. However, it is possible to estimate the order of $Pr(A^-)$ by the differences of reactivity of A^- with TCNE (Table I), which gives $Pr(PMMA^-) < Pr(PP^-) < Pr(PE^-) < Pr(PVDF^-) < Pr(PTFE^-)$, where $PMMA^-$, PP^-, PE^-, $PVDF^-$, and $PTFE^-$ are the mechanoanions of PMMA, PP, PE, PVDF, and PTFE. The order of the polymers from low $Pr(A^-)$ to high is PMMA–PP–PE–PVDF–PTFE (Table II).

Table II
Relationship between the Molecular Structures of Polymers and the Order of $Pr(A^-)$, $Ea(B^\bullet)$, and the Estimated Sign of the Charge Induced by Friction on the Polymer Surface

polymer	molecular structure	order of $Pr(A^-)$	order of $Ea(B^\bullet)$	speculated sign of charge
PMMA	$-(CH_2C(CH_3)(COOCH_3))_n-$	low	low	+
PP	$-(CH_2CH(CH_3))_n-$	↓	↓	
PE	$-(CH_2CH_2)_n-$			
PVDF	$-(CH_2CF_2)_n-$			
PTFE	$-(CF_2CF_2)_n-$	high	high	-

A similar order of $Pr(A^-)$ to that indicated above can be presumed from the molecular structure from the assumption that A^- with substituents with more electron-donating groups or atoms can more easily release an electron than that with less electron-donating groups.

It is reported[18] that trifluoromethyl radical ($CF_3^\bullet$) and ethyl radical ($C_2H_5^\bullet$) have molecular electron affinities of 2.01 and 0.34 eV, respectively. It can be assumed that a radical having substituents with a high atomic electron affinity, for example, fluorine atom with 3.399 eV,[18] attracts an electron more strongly than substituents with a low atomic electron affinity, for example, hydrogen atom with 0.754209 eV.[18]

The following electron attractive reaction of $B^\bullet$ is suggested:

$$B^\bullet + e^- \rightarrow B^- \qquad (5)$$

The electron affinity of $B^\bullet$ is called $Ea(B^\bullet)$ in this article. The $B^\bullet$ having substituents with a high atomic electron affinity could have high $Ea(B^\bullet)$. Accordingly, the order of $Ea(B^\bullet)$ is given by the molecular structure: $Ea(PP^\bullet) < Ea(PE^\bullet) < Ea(PVDF^\bullet) < Ea(PTFE^\bullet)$, where $PP^\bullet$, $PE^\bullet$, $PVDF^\bullet$, and $PTFE^\bullet$ are mechanoradicals of PP, PE, PVDF, and PTFE. The order of the polymers from low $Ea(B^\bullet)$ to high $Ea(B^\bullet)$ is thus PP–PE–PVDF–PTFE (Table II).

When polymers having a relatively low $Pr(A^-)$ to high $Pr(A^-)$ are arranged, the polymer series, PMMA–PP–PE–PVDF–PTFE, is identical with the series from the polymer having relatively low $Ea(B^\bullet)$ to high $Ea(B^\bullet)$. According to the definitions of the electron-release potential of the mechanoanion and the electron affinity of the mechanoradical, this coincidence is reasonable.

Here we consider a generation mechanism of triboelectricity due to the production and the reaction of mechanoanions and mechanoradicals of polymers A and B. When board A composed of polymer A and board B composed of polymer B are rubbed against each other, A^- is produced on the surface by a heterolytic carbon–carbon bond scission of the main chain of polymer A, and $B^\bullet$ is produced by a homolytic carbon–carbon bond scission of the main chain of polymer B. A^- donates an electron, and $B^\bullet$ accepts the electron released from A^- by frictional contact. The charge carrier is an electron. The charge separation is induced by electron transfer from A^- in polymer A to $B^\bullet$ in polymer B. Polymer A becomes positively charged, and polymer B becomes negatively charged. An electron-transfer reaction from A^- to $B^\bullet$ is suggested as follows:

$$A^- + B^\bullet \rightarrow A^\bullet + B^- \qquad (6)$$

which constitutes charge separation by an electron transfer.

A polymer located near PMMA in the series donates an electron easily due to low Pr but accepts an electron with difficulty and due to low Ea could therefore be positively charged. In contrast, a polymer located near PTFE accepts a donated electron easily due to high Ea but donates an electron with difficulty due to high Pr and could therefore be negatively charged.

The polymer series proposed here, PMMA–PP–PE–PVDF–PTFE, is identical with the well-known triboelectric series of polymers.[19,20]

We conclude that a generation mechanism of triboelectricity in polymers is due to an electron-transfer reaction from the mechanoanions to the mechanoradicals that are produced by mechanical fracture of the main chains of polymers via friction. The sign of the charge induced by friction can be estimated from $Pr(A^-)$ and $Ea(B^\bullet)$, i.e., the molecular structure of each polymer. The triboelectric series proposed, PMMA–PP–PE–PVDF–PTFE, in which polymers having a relatively low $Pr(A^-)$ to high $Pr(A^-)$ or low $Ea(B^\bullet)$ to high $Ea(B^\bullet)$ are arranged, is identical with the well-known triboelectric series. The triboelectric series suggests an order of $Pr(A^-)$ and $Ea(B^\bullet)$ in these polymers.

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Masato Sakaguchi*

Ichimura Gakuen Junior College
61 Uchikubo, Inuyama 484, Japan

Shigetaka Shimada and Hisatsugu Kashiwabara*

Nagoya Institute of Technology
Gokiso-cho, Showa-ku, Nagoya 466, Japan

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