

## Preparation and Properties of Polymer Hybrids Containing Nanoparticles with Controlled Interfacial Structure

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Polystyrene (PS)-grafted-titanium oxide (TiO<sub>2</sub>) nanoparticles with diameter of 15 nm were prepared by using 'grafting-from' surface modifier with nitroxide-mediated radical polymerization (NMRP) initiator. The graft densities were relatively high (0.04-0.28 chains/nm<sup>2</sup>) compared with the 'grafting-to' method (<0.01 chains/nm<sup>2</sup>). PS-grafted-TiO<sub>2</sub> nanoparticles were stably dispersed in good solvents for polymer chain due to the steric repulsion among grafted chains derived from osmotic pressure effect and affinity for solvents. After PS-grafted-TiO<sub>2</sub> particles were added in CHCl<sub>3</sub> with PS, hybrid films were prepared by solvent casting. The PS-grafted-TiO<sub>2</sub>/PS hybrid films showed high transmittance in the visible light region accompanying ultraviolet absorption characteristics of TiO<sub>2</sub> due to the dispersion of nanoparticles in PS matrix. Dynamic storage modulus, E' of the hybrid film was approximately 1.20 times as high as that of PS film at 323K. Furthermore, friction test revealed that wear resistance of PS-grafted-TiO<sub>2</sub>/PS hybrid thin films improved compared with PS film.

Key words: Surface grafting, Surface density, Living radical polymerization, Titanium oxide

### 1. INTRODUCTION

The modification of substrate surfaces with thin polymer films is widely used to control surface properties such as wettability, biocompatibility, corrosion resistance and friction. On the other hand, polymer composite materials with nanoparticles as fillers are generating interest in several applications. In this case, since the dispersion of nanoparticles to the polymer matrix originates from the affinity between nanoparticle surface and polymer matrix, appropriate surface modification method should be employed. This method achieves the stable dispersion of nanoparticles in a matrix. However, previously the modification on nanoparticle surface was performed by adsorbing the organic molecule with high affinity to matrix because it is impossible to technically modify surface with polymer thin film.

Recently, a 'grafting-from' method has been used to carry out the direct polymerization on nanoparticle surfaces [1,2]. Polymers with reactive end groups can be grafted onto surfaces, resulting in so-called polymer brushes [3,4]. The advantage of polymer brushes over other surface modification methods is their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility towards the introduction of a variety of functional groups.

Previously, the authors have reported the direct polymerization of styrene from the nitroxyl-mediated radical polymerization initiator with phosphoric acid immobilized on the magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticle surface [5,6,7]. Although magnetite particles easily aggregates due to strong magnetic interaction,

polystyrene-grafted-magnetite particles were stably dispersed in good solvents but not stably in poor solvents.

Titanium oxide (TiO<sub>2</sub>) exhibits various properties such as the high refractive index, UV light absorption, and photocatalytic activity exploited for practical applications stood for the photocleavage of water [8] and solar cell [9]. In particular, rutile type TiO<sub>2</sub> was used for white pigment due to hiding power. Thus, solutions with rutile type TiO<sub>2</sub> that the size is generally more than micrometer are very white, not transparent.

In this paper, 'grafting-from' surface modification was applied to TiO<sub>2</sub> nanoparticle. Direct polymerization of PS on TiO<sub>2</sub> nanoparticles was performed, and the dispersibility of the polymer-grafted-TiO<sub>2</sub> and in various solvents was investigated. Furthermore, the preparation and characterization of polymer nanohybrid with polymer-grafted-TiO<sub>2</sub> were performed.

### 2. EXPERIMENTAL

#### 2.1 Materials

Styrene was obtained from WAKO Pure Chemical Industries, Ltd. and purified by distillation under reduced pressure over calcium hydride. TiO<sub>2</sub> particles with diameters of approximately 15 nm were given by TAYCA Corporation. Nitroxide-mediated radical polymerization initiator was synthesized according to the previous report [7]. The designed surface initiator has both a living free radical polymerization moiety that contains 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) and a phosphoric acid moiety that can interact with Ti-OH groups on nanoparticle surface.

Table I. Reaction conditions and characteristics of PS-grafted-TiO<sub>2</sub>

| entry | conv. % | monomer/free initiator | $M_n$ , free | $M_w/M_n$ | graft density chains/nm <sup>2</sup> | Participated initiator moiety / % |
|-------|---------|------------------------|--------------|-----------|--------------------------------------|-----------------------------------|
| 1     | 81.2    | 523:1                  | 10100        | 1.45      | 0.17-0.28                            | 28                                |
| 2     | 87.5    | 523:1                  | 18800        | 1.29      | 0.10-0.17                            | 17                                |
| 3     | 97.0    | 523:1                  | 32100        | 1.33      | 0.06-0.10                            | 10                                |
| 4     | 83.1    | 872:1                  | 51900        | 1.35      | 0.05-0.09                            | 8                                 |
| 5     | 90.7    | 872:1                  | 63800        | 1.40      | 0.04-0.06                            | 6                                 |

## 2.2 Surface-Initiated polymerization of styrene on TiO<sub>2</sub> nanoparticle

Polymerization of styrene on the surface of nanoparticles was carried out by heating a mixture of surface initiator modified TiO<sub>2</sub> particles, free initiator (4-hydroxy-1((2'-hydroxy-1'-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine) [10], and monomers, after degassing by four freeze-pump-thaw cycles. Free initiator was used to control of the number-average molecular weights ( $M_n$ ) by changing a ratio for monomer.

## 2.3 Measurements

Gel permeation chromatographic (GPC) analysis was carried out at 313 K on a Tosoh HLC-8120GPC with a guard column (Shodex GPC KF-804L), and a differential refractometer RI-8020. Tetrahydrofuran (THF) was used as an eluent for PS analysis. PS standards were used to calibrate the GPC system. Thermogravimetric analysis (TGA) was performed by TG 8120 (Rigaku Corporation), using aluminum pan, under a nitrogen atmosphere and a heating rate of 10 K/min. Ultraviolet-visible (UV-vis) absorption spectra were recorded by Lambda 35 (Perkin Elmer Japan Co., Ltd.). Transmission electron microscopic (TEM) observation was made on an H-7500 (Hitachi) operated at 100 kV. Dynamic light scattering (DLS) measurement was performed by DLS-7000 (Otsuka Electronics CO., LTD.) at 20-40 mW of Ar laser. Dynamic viscoelastic measurement was recorded by RHEOVIBRON DDV-01FP (Orientec A&D Co., Ltd.) under a nitrogen atmosphere and a heating rate of 2 K/min. Friction and wear tests of PS thin films were carried out on a conventional ball-on-disk type friction tester (SHINTO Scientific Co., Ltd.) in air at 298 K, rate 80 mm/min. A 5.0-mm-radius ball made of stainless steel was slid on a disk. The friction coefficient was determined by the distortion of a strain gauge attached to the arm of the tester and was recorded as a function of time.

## 3. RESULTS AND DISCUSSION

### 3.1 Determination of graft density of surface polymer on TiO<sub>2</sub> nanoparticle

Table I shows the number-average molecular weights ( $M_n$ ), polydispersities ( $M_w/M_n$ ), and graft densities  $\sigma$  (chains/nm<sup>2</sup>) of representative PS on TiO<sub>2</sub> particles.  $M_n$  and  $M_w/M_n$  were evaluated by GPC. The graft densities were calculated from the weight loss of polymer on nanoparticles by TGA, and the surface area of TiO<sub>2</sub> was estimated assuming TiO<sub>2</sub> particles to be spheres with diameters of 15 nm and densities of 2.5-4.2 g/cm<sup>3</sup> for a whole particle. These graft densities were relatively high compared with the 'grafting-to' method (<0.01 chains/nm<sup>2</sup>). The density of surface immobilized initiator was 0.6-1.0 molecules/nm<sup>2</sup>. It therefore can be concluded that 6-36 % of initiator molecules on the particles surface participated in the polymerization.

### 3.2 The dispersibility of PS-grafted-TiO<sub>2</sub> nanoparticle in organic solvents

To investigate the modification effects, UV absorption

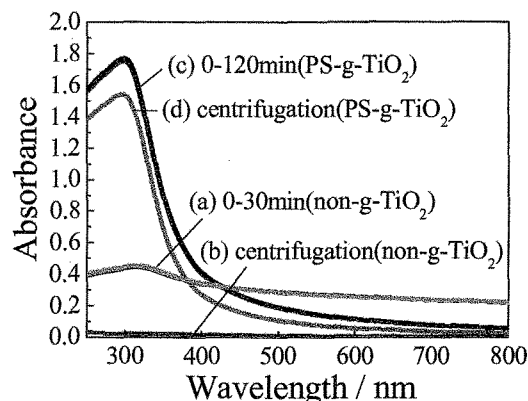


Fig. 1 UV-vis spectra of (a,b) non-grafted-TiO<sub>2</sub> and (c,d) PS-grafted-TiO<sub>2</sub> in chloroform (0.05 mg/mL).

measurement was performed. PS-grafted-TiO<sub>2</sub> nanoparticle ( $M_n$  18800,  $M_w/M_n$  1.29) was added to chloroform and dispersed by sonication ( $\nu = 38$  kHz, 200 W) for 10 min. Fig. 1 shows UV-vis spectra of non-grafted and PS-grafted-TiO<sub>2</sub> ( $M_n$  18800,  $M_w/M_n$  1.29) in chloroform. In the case of non-grafted-TiO<sub>2</sub>, UV spectra showed peak (at  $\lambda_{max} = 308$  nm) with UV-light absorption and light scattering caused by the aggregation. Although TiO<sub>2</sub> is nanometer scale single particle, when aggregated in solvent, it becomes the micrometer scale and the suspension looks white. After centrifugation at 3500 rpm for 20 min, the peak disappeared due to the precipitation of particles to the bottom of the UV cell. On the other hand, in the case of PS-grafted-TiO<sub>2</sub>, UV-vis spectra showed UV-light absorption peak (at  $\lambda_{max} = 294$  nm) without strong light scattering. Additionally, the difference of absorbance between visible region and ultraviolet region was very large. The spectra did not change over several hours. Even after centrifugation, light scattering slightly decreased with keeping UV-light absorption peak. In

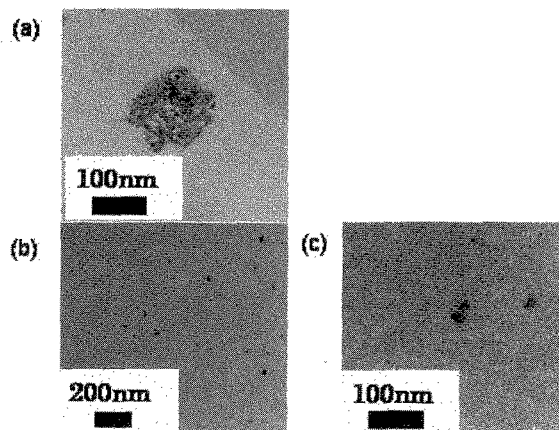


Fig. 2 TEM images of (a) non-grafted-TiO<sub>2</sub> and (b, c) PS-grafted-TiO<sub>2</sub> ( $M_n$  18800) dispersed from chloroform solution (0.01 mg/mL).

other good solvents such as tetrahydrofuran (THF), toluene and ethyl acetate, PS-grafted-TiO<sub>2</sub> nanoparticles were stably dispersed. On the other hand, in poor solvents such as acetone, methanol and ethanol, the nanoparticles were not stably dispersed. This result shows the stable dispersion is due to the steric repulsion among polymer chains affected from osmotic pressure and affinity of surface polymer chains against solvent. It seems that the dispersibility and stability were strongly influenced by solubility of the grafted polymer on TiO<sub>2</sub> nanoparticle surface.

Fig. 2 shows transmission electron microscopic (TEM) images of non-grafted-TiO<sub>2</sub> and PS-grafted-TiO<sub>2</sub> particles in chloroform prepared by dropping their dispersion after sonication onto a carbon-coated copper grid. Non-grafted-TiO<sub>2</sub> nanoparticles were observed as an aggregate over several hundred nanometers. In contrast, PS-grafted-TiO<sub>2</sub> nanoparticles were observed to have fine dispersion as one or two particles. These findings clearly revealed that the surface-initiated polymerization of styrene from TiO<sub>2</sub> nanoparticles allows for dispersion and stability in appropriate solvents. Additionally, from dynamic light scattering (DLS) measurements, dispersion states of PS-grafted-TiO<sub>2</sub> in chloroform were distributed  $89 \pm 10$  nm at 0.01 mg/mL. A calculated diameter of a PS-grafted-nanoparticle was about 45 nm [11]. From the comparison of the size of nanoparticle in TEM image and DLS measurement with calculated value, PS-grafted-TiO<sub>2</sub> nanoparticles were dispersed as one or two particles.

### 3.3 The dispersibility of PS-grafted-TiO<sub>2</sub> nanoparticle in PS matrix

To characterize the dispersibility of PS-grafted-TiO<sub>2</sub> nanoparticles in PS matrix, PS hybrid film was prepared. PS hybrid films were prepared by casting from chloroform with non-grafted or PS-grafted-TiO<sub>2</sub> and PS ( $M_n$  96000, polydispersity). The film thickness was 80-100  $\mu$ m. In these  $M_n$  listed in Table I, cast film by using PS matrix polymerized from free initiator could not be prepared because of high brittleness resulting from small  $M_n$  and relatively narrow  $M_w/M_n$ .

Fig. 3 shows transmittance of PS films with non-grafted-TiO<sub>2</sub> or PS-grafted-TiO<sub>2</sub> ( $M_n$  18800,  $M_w/M_n$  1.29) particles. When non-grafted-TiO<sub>2</sub> particles were added into PS matrix, the film showed decrease of transmittance and ultraviolet absorption was not observed (curve4 in Fig.3). On the other hand, in the case of PS films with PS-grafted-TiO<sub>2</sub> 0.05 wt% (curve2 in Fig3.) and 0.15 wt% (curve3 in Fig3), the films showed high transmittance in the range of visible region accompanying ultraviolet absorption characteristic of TiO<sub>2</sub> in the ultraviolet region. From optical microscopy,

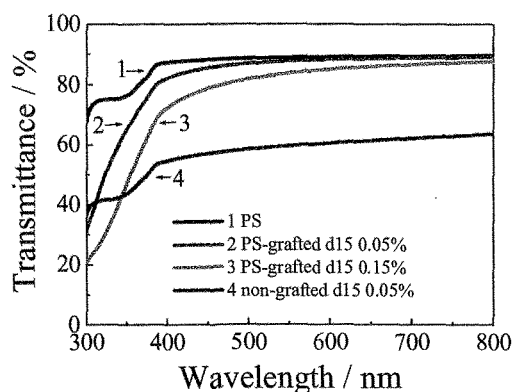


Fig. 3 Transmittance of PS films with non-grafted-TiO<sub>2</sub> and PS-grafted-TiO<sub>2</sub>.

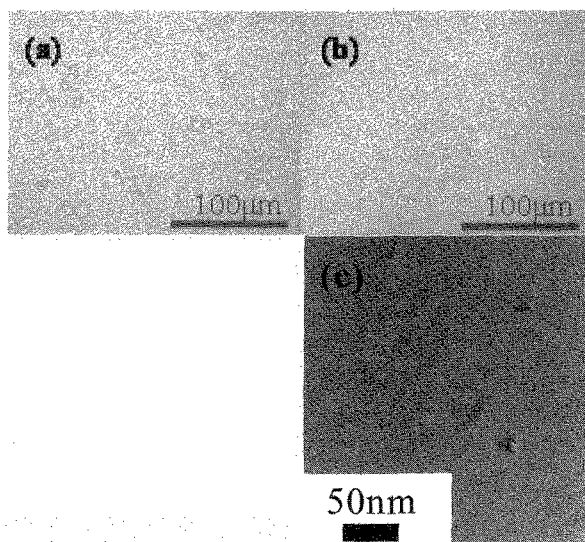


Fig. 4 Optical micrographs of PS films with (a) non-grafted-TiO<sub>2</sub> and (b) PS-grafted-TiO<sub>2</sub> (0.05 wt%) and TEM image of (c) PS film with PS-grafted-TiO<sub>2</sub>.

in the case of PS films with non-grafted-TiO<sub>2</sub>, several  $\mu$ m aggregations that cause decrease of transmittance were observed (Fig4.(a)). On the other hand, in PS films with PS-grafted-TiO<sub>2</sub> 0.05 wt%(Fig4.(b)), aggregations with several  $\mu$ m were not observed due to compatibility of surface PS graft chains for PS matrix. After the film was embedded with epoxy resin and cut by microtome with diamond knife, TEM observation was performed. From TEM observation, finely dispersed TiO<sub>2</sub> particles were observed in PS matrix (Fig4.(c)).

### 3.4 Dynamic viscoelastic measurement of PS film with PS-grafted-TiO<sub>2</sub>

Fig. 5 shows temperature dependence of dynamic storage modulus  $E'$ . Table II indicates average  $E'$  value of PS films at 273 K and 323 K. As a result,  $E'$  of PS film with non-grafted-TiO<sub>2</sub> did not change by little addition of TiO<sub>2</sub> nanoparticle. On the other hand,  $E'$  of PS films

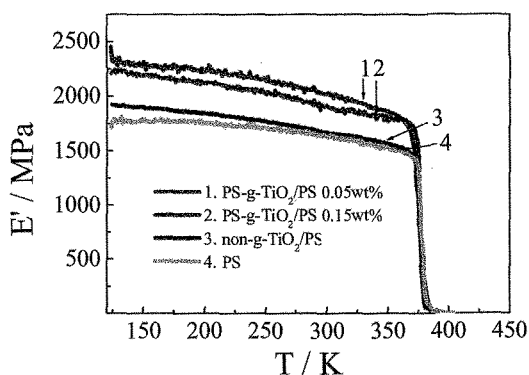


Fig. 5 Temperature dependence of dynamic storage modulus,  $E'$  of PS films with non-grafted-TiO<sub>2</sub> and PS-grafted-TiO<sub>2</sub> at 11Hz.

Table II.  $E'$  of PS films

| entry | sample                             | $E'$ /MPa (273 K) | $E'$ /MPa (323 K) |
|-------|------------------------------------|-------------------|-------------------|
| 1     | PS-g-TiO <sub>2</sub> /PS 0.05wt%  | 2130              | 1980              |
| 2     | PS-g-TiO <sub>2</sub> /PS 0.15wt%  | 2060              | 2060              |
| 3     | non-g-TiO <sub>2</sub> /PS 0.05wt% | 1720              | 1630              |
| 4     | PS                                 | 1760              | 1610              |

with 0.05–0.15 wt% PS-grafted-TiO<sub>2</sub> was approximately 1.20–1.23 times high at 323 K compared with that of PS film. However,  $\tan\delta$  peak reduction and shift of  $\alpha_a$  adsorption were not clearly observed because of the weak interaction between grafted PS chain and PS matrix owing to the  $\theta$  solvent characteristics of matrix PS.

### 3.5 Friction test of PS thin films with PS-grafted-TiO<sub>2</sub>

Furthermore, to investigate the effect of PS-grafted-TiO<sub>2</sub> on frictional properties of PS film, friction and wear tests were performed. PS thin films were prepared on hydrophilic silicon wafer (20 x 30 mm) by spin coating from 4 wt% toluene solution. In the case of PS thin films with PS-grafted-TiO<sub>2</sub> preparation, PS polymerized from free initiator that has same  $M_n$  of PS grafted from TiO<sub>2</sub> surface was used as a matrix. Table III shows condition of PS thin hybrid films. Fig. 6 indicates friction cycle dependence of PS film and PS-grafted-TiO<sub>2</sub> at 50 g load. Friction coefficient of PS thin film rapidly increased around 25 cycles and reached almost 0.45. This means that PS thin film was removed by heat of abrasion and stainless steel ball reached silicon wafer substrate. Friction coefficient of PS thin films with PS-grafted-TiO<sub>2</sub> slowly increased compared with that of PS thin film as increasing friction cycles, although all PS thin films were removed and silicon wafer appeared eventually. Therefore, wear resistance increased due to

Table III. Condition of PS hybrid films

| entry | sample                  | Thickness(nm) | $M_n$ | $M_w/M_n$ | TiO <sub>2</sub> (wt%) |
|-------|-------------------------|---------------|-------|-----------|------------------------|
| 1     | PS                      | 254           | 4400  | 1.04      | -                      |
| 2     | PS-TiO <sub>2</sub> /PS | 275           | 6800  | 1.40      | 0.15                   |
| 3     | PS-TiO <sub>2</sub> /PS | 258           | 5190  | 1.35      | 0.28                   |

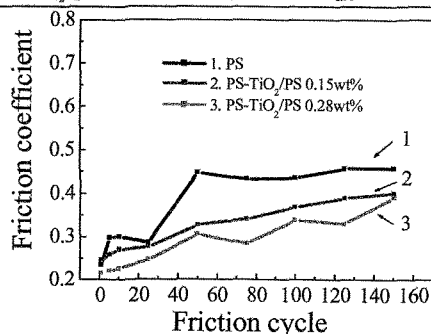


Fig. 6 Friction cycle dependence of PS film and PS films with PS-grafted-TiO<sub>2</sub> at load 50 g.

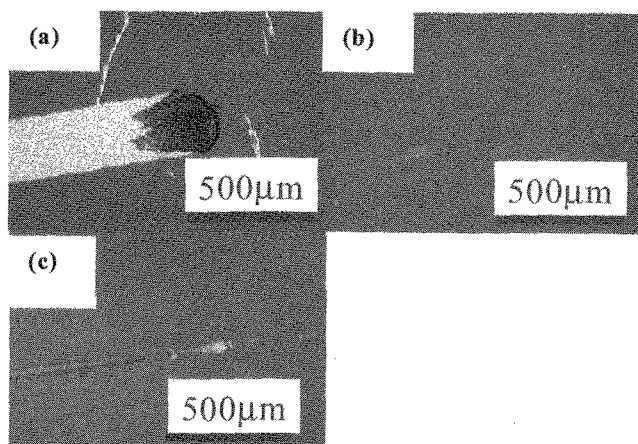


Fig. 7 Optical micrographs of surface of PS thin films after 5 cycles. (a) PS thin film, (b) PS thin film with PS-grafted-TiO<sub>2</sub> (0.15 wt%), (c) PS thin film with PS-grafted-TiO<sub>2</sub> (0.28 wt%).

the addition of PS-grafted-TiO<sub>2</sub>. Regarding wear resistance mechanism, it is considered that TiO<sub>2</sub> transmitted load accompanying reduction of friction coefficient due to the presence of grafted PS layer.

Fig. 7 shows optical micrograph of PS thin films after 5 cycles. Optical micrograph of PS thin film was observed friction trace with about 250 µm width and silicon wafer surface. On the other hand, in the case of PS thin film with PS-grafted-TiO<sub>2</sub>, although friction traces with about 36 µm width were observed, silicon wafer surface did not appear. This also indicates improvement of wear resistance.

## 4. CONCLUSION

In conclusion, TiO<sub>2</sub> nanoparticles grafted high density PS brush were stably dispersed in good solvents for polymer chain due to the steric repulsion among grafted chains derived from osmotic pressure effect and affinity for solvents. The PS-grafted-TiO<sub>2</sub> dispersed as one or two particles in good solvents. When the PS-grafted-TiO<sub>2</sub> particles are finely dispersed, the difference of absorbance between visible region and ultraviolet region is ten times or more as large as that of non-grafted-TiO<sub>2</sub>. The PS film with PS-grafted-TiO<sub>2</sub> showed high transmittance in the range of visible light region accompanying ultraviolet absorption characteristic due to dispersion of TiO<sub>2</sub> nanoparticles in PS matrix. Dynamic storage modulus,  $E'$  of the hybrid film was approximately 1.20–1.23 times high at 323K compared with that of PS film. Furthermore, friction test revealed that wear resistance of PS hybrid thin films with PS-grafted-TiO<sub>2</sub> improved compared with PS film.

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- [11]The height  $h$  of the grafted layer in good solvents is given by  $h = (12/\pi)^{1/3} N \sigma^{1/3} (\omega/v)^{1/3}$  where  $\omega$  is the excluded volume parameter, approximately  $(2 \text{ \AA})^3$ ;  $N$  is the number of monomers; and  $v = (a^3/3)^{-1}$ ,  $a$  is the Kuhn statistical segment length with  $a = 0.67 \text{ nm}$  for a polystyrene monomer unit. Eq. was listed in: R. Jordan, A. Ulman, J. F. Kang, M. H. Rafailovich, . Sokolov, *J. Am. Chem. Soc.*, **121**, 1016(1999).

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