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Viscoelasticity, Leachability, and Antimicrobial Activity of Poly(vinyl chloride) Blended with Benzyldimethyltetradecylammonium Bis(2-ethylhexyl) Sulfonatosuccinate

Hajime Katano*[1] **and Toshihide Tsukatani**[2]

[1]Department of Bioscience, Fukui Prefectural University, Eiheiji-cho, Fukui 910-1195

[2]Research and Development Division, Nicca Chemical Co., Ltd., Bunkyo, Fukui 910-8670

Received July 16, 2009; E-mail: hajime@fpu.ac.jp

Benzyldimethyltetradecylammonium ($BA14^+$) salt with bis(2-ethylhexyl) sulfonatosuccinate ($BEHS^-$) anion maintains its liquid state even at room temperature, so it can be regarded as a halogen-free low-volatile liquid material. In this study, the potential use of BA14BEHS as additive for poly(vinyl chloride) (PVC) has been investigated. The temperature dependence of the storage and loss moduli of PVC films blended with BA14BEHS showed a similar trend of that with a traditional plasticizer bis(2-ethylhexyl) phthalate. The glass transition temperature of the PVC films determined as the peak top temperature in loss modulus was lowered with increasing BA14BEHS content. The 10% BA14BEHS-blended PVC film was placed in contact with water and heptane, but BA14BEHS could not be detected from the aqueous and organic media. The results indicate that BA14BEHS can be applied as a plasticizer for PVC. Since BA14BEHS can be used to give textiles antimicrobial properties, the activity of the BA14BEHS-blended PVC film was assayed against *Escherichia coli* JM109. In spite of the low-leachability of BA14BEHS, the PVC film showed a significant antimicrobial activity.

Room temperature molten salts or ionic liquids (RTILs) have attracted attention as alternatives to conventional organic solvents because they have unique properties such as low volatility and low flammability. Attention has also been toward their application as performance additives.[1–3] Recently, the use of RTILs as plasticizers for poly(methyl methacrylate)[4,5] and poly(vinyl chloride)[6] (PVC) has been suggested to replace traditional phthalate esters.

In a previous paper,[7] it has been shown that benzyldimethyltetradecylammonium ($BA14^+$, Figure 1a) salt with bis(2-ethylhexyl) sulfonatosuccinate ($BEHS^-$, Figure 1b) anion maintains its liquid state even at room temperature. Because BA14BEHS is a halogen-free low-volatile liquid material, it can be expected to be used advantageously in place of traditional polymer additives. This paper describes the physicochemical properties of BA14BEHS and a comparison with a traditional plasticizer bis(2-ethylhexyl) phthalate (DEHP) and conventional RTILs. The BA14BEHS exhibited a low glass transition temperature (T_g) and a high temperature stability. Thus BA14BEHS-blended PVC films have been prepared, and the viscoelastic property, leachability, and surface resistivity have been studied. The experimental results are described in this paper. The BA14BEHS exhibited a good compatibility with PVC and a low-leachability, indicating that BA14BEHS can be applied as a plasticizer from the viewpoint of physicochemical properties.

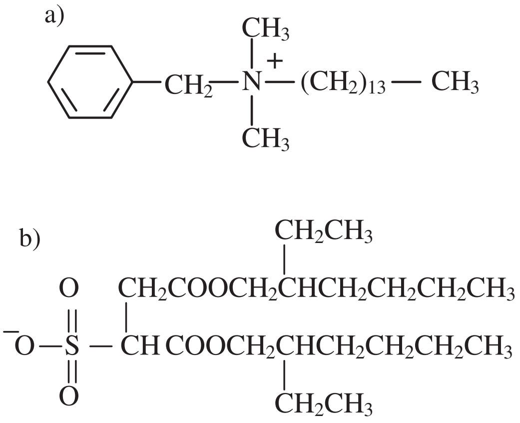

Figure 1. Chemical structure of a) benzyldimethyltetradecylammonium ($BA14^+$) cation and b) bis(2-ethylhexyl) sulfonatosuccinate ($BEHS^-$) anion.

BA14BEHS can be prepared by the anion exchange of benzyldimethyltetradecylammonium chloride (BA14Cl). BA14Cl has been considered to be one of the safest antimicrobial agents and has a long history of efficacious use.[8,9] In the previous study,[7] it has been shown that textile products treated with BA14BEHS exhibited high antimicrobial activities. The present paper also describes the results of an antimicrobial test with BA14BEHS-blended PVC film. The BA14BEHS-blended PVC film showed a significant antimicrobial activity against *Escherichia coli* JM109, indicating the feasibility of BA14BEHS as an immobilized antimicrobial agent for PVC.

Experimental

Chemicals. BA14BEHS was prepared as follows: 20 mmol of benzyldimethyltetradecylammonium chloride (Tokyo Chemical

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Industry) and 20 mmol of sodium bis(2-ethylhexyl) sulfonatosuccinate (Aldrich) were mixed in 200 mL of water. The mixture was heated with stirring until the solid substances were dissolved completely. The stirring was stopped, and then the mixture separated into an oily substance and an aqueous phase. The mixture was transferred into a separating funnel, and the aqueous phase was removed. The crude BA14BEHS was purified by shaking with water several times. The BA14BEHS was dried at 80 °C under 50 mmHg until the water content became 1% or less. The BA14BEHS was confirmed by IR and UV spectra.[7]

Bis(2-ethylhexyl) phthalate (Wako) was used as a reference material. Poly(vinyl chloride) powder ($n = 1100$) and tetrahydrofuran (with stabilizer) were obtained from Wako, and were used to prepare the sample PVC films as follows: The PVC powder and the BA14BEHS were dissolved in tetrahydrofuran. The mixture was put into a glass petri dish, and was dried in atmospheric pressure to cast the sample PVC films. The sample films were dried at 1 mmHg and 110 °C for 1 h to evaporate tetrahydrofuran completely. Except for the dynamic mechanical analysis, the PVC films were examined stuck to the glass dishes.

Other chemicals were reagent-grade materials and were used without further purification.

Apparatus. Differential scanning calorimetric (DSC) analysis was performed with a SII Nanotechnology DSC6220 at 10 °C min^{-1} heating rate. Thermogravimetric analysis (TGA) was performed with a Shimadzu TG-50 at 10 °C min^{-1} heating rate, under nitrogen flow of 50 mL min^{-1}. A vibro viscometer (A&D SV-10), a conductivity meter (DKK-TOA CM-40V), and a Karl Fischer titrator (Hiranuma Sangyo AQV-5) were used for the determination of the viscosity, conductivity, and water content, respectively. The experiments were performed at 25 ± 1 °C.

The elastic moduli of the BA14BEHS-blended PVC films were evaluated using a dynamic mechanical analyzer (SII Nanotechnology, DMS120) for a temperature range from −130 to nearly 150 °C with a 5 °C min^{-1} heating rate at a frequency of 10 Hz. The surface resistivity of the BA14BEHS-blended PVC films was determined with an electrometer (ADCMT 8340A) at 20 °C and 40% relative humidity.

Leachablility. A 40 mL aliquot of distilled water or heptane was put into glass petri dishes (76 mm inner diameter) in which the PVC film (ca. 0.04 mm thickness) was cast on the bottom. The water or heptane samples were in contact with the PVC film at a given temperature and contact time. The water sample was condensed 10 fold. The heptane sample was mixed with a 1/10 volume of distilled water, and heptane was evaporated. These aqueous media and 1:2 (volume ratio) water–acetonitrile (W–AN) solution containing 13.3 mM CH_3COOH, 13.3 mM CH_3COONa were mixed at the volume ratio of 1:3 to prepare the 1:1 W–AN media.

In this study, the amount of released additives in the sample W–AN media was determined by capillary electrophoresis.[10] A capillary electrophoresis system (Otsuka Electric, CAPI-1000) was used for the determination. The applied voltage was held at 40 kV. The column was a fused-silica capillary with a total length of 75 cm and an effective length of 52 cm (75 µm i.d.). The temperature of the capillary cartridge during electrophoresis was maintained at 25 °C and UV detection was done at 220 nm. Samples were loaded by pressure injection for 3 s.

Antimicrobial Test. The antimicrobial performance of the PVC films was examined according to JIS Z2801[11] with *E. coli* JM109. The bacterial cells were grown at 37 °C with shaking in LB medium, and were diluted to a density of 2.5–10 × 10^5 cells mL^{-1}. 50 µL of the suspension was put on the PVC films, and remained in contact for 24 h at 37 °C. The bacterial medium was washed off with 3 mL of LB medium. 50 µL of the LB medium was put on an agar plate, and the bacterial cells were grown at 37 °C for 24 h. Then the number of colonies (N) in the agar plate was estimated. The N-values refer to those obtained simultaneously from the pure PVC film (N_{std}).

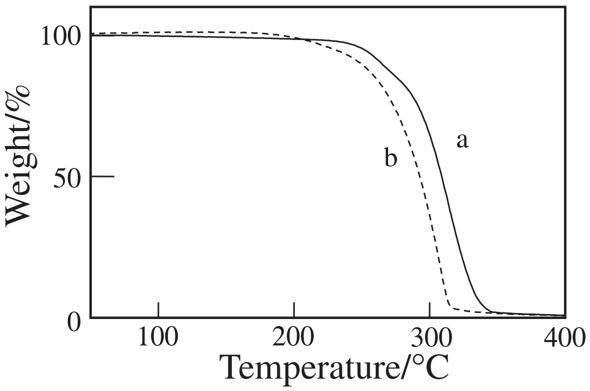

Figure 2. TGA curves of (a) BA14BEHS and (b) DEHP.

Results and Discussion

Physicochemical Properties. The BA14BEHS did not display solid–liquid phase transition but a glass transition in the DSC curve. The glass transition temperature was determined to be $T_g = -16$ °C. On the other hand, DEHP has a melting point of −50 °C.[12,13] Curve a in Figure 2 shows the TGA curve of BA14BEHS. The BA14BEHS exhibited thermal stability up to ca. 270 °C. Thus, BA14BEHS maintains in liquid state over wide temperature range. Curve b in Figure 2 shows the TGA curve of DEHP. The high temperature stability of BA14BEHS was higher than DEHP.

The viscosity of BA14BEHS was determined to be 14800 mPa s at 25 °C, which is much higher than that of DEHP[12] (56.5 mPa at 25 °C). This may be one of the reasons why the plasticizing effectiveness of BA14BEHS was estimated to be lower than that of DEHP as described below. Also, the viscosity of BA14BEHS is much higher than conventional RTILs such as imidazolium-based ionic liquid[14] and quaternary ammonium–bis(fluoroalkylsulfonyl)imide,[15] suggesting that the ionic association of the $BA14^+$ cation and the $BEHS^-$ anion is not weak. The conductivity was determined to be 0.002 mS cm^{-1} at 25 °C, which is much lower than conventional RTILs. The density of BA14BEHS was 0.99$_2$ g cm^{-3} at 25 °C, which is close to that of 0.979 g cm^{-3} for DEHP.[12] The density is much lower than that of PVC resin, so that BA14BEHS may be separated from PVC in recycling process.[16]

The BA14BEHS, as well as DEHP, is immiscible in water. However, since BA14BEHS can be dispersed stably in aqueous media, the solubility of BA14BEHS in water could not be determined exactly. Aqueous medium was emulsified by addition of BA14BEHS even at 0.01 wt % level. Therefore the solubility of BA14BEHS in water may be compared with that of DEHP (<0.01 wt % and 0.4–400 µg dm^{-3} in Refs. 12 and 13, respectively). The solubility of water in BA14BEHS was determined to be 3.5 wt %. The solubility is higher than that of 0.20 wt % for DEHP,[12] but can be compared with those of the conventional water-immiscible RTILs.[14,15] The water-

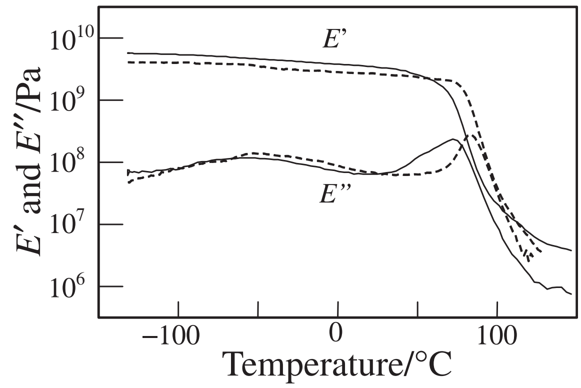

Figure 3. Storage (E') and loss (E'') moduli of the 0% (dashed lines) and 10% (solid lines) BA14BEHS-blended PVC films.

immiscibility may be one of the reasons why BA14BEHS did not exhibit antistatic effect as described below. The BA14BEHS is also immiscible with non-polar solvents such as paraffin, but is miscible with polar organic solvents, so that BA14BEHS-blended PVC films can be prepared with the tetrahydrofuran solution.

Viscoelasticity. Dashed lines in Figure 3 show the temperature dependence of storage (E') and loss (E'') moduli of PVC film which does not contain a plasticizer, that is, 0% BA14BEHS-blended PVC film. The E' decreased remarkably at around 80 °C. On the other hand, E'' increased to a peak around the temperature and then dropping back down. By taking as the peak top temperature in E'', the glass transition temperature was determined to be $T_g(E''_{max}, 10\,Hz) = 82$ °C.

No liquid material leaching out was observed visually at the surface of 10% BA14BEHS-blended PVC film, so that the BA14BEHS at the content appeared to be compatible with PVC resin. The temperature dependence of E' and E'' of the 10% BA14BEHS-blended PVC film is shown by the solid lines in Figure 3. By addition of BA14BEHS, the E' began to decrease and the E'' showed a peak at lower temperature than those of 0% BA14BEHS-blended PVC film. Also the peak-shape of E'' became broader than that of 0% BA14BEHS-blended PVC film. The effect of BA14BEHS on the viscoelasticity of PVC film is similar to that of DEHP.[17] The $T_g(E''_{max}, 10\,Hz)$ of the PVC film was lowered by addition of 5, 10, and 20% BA14BEHS as listed in Table 1, indicating that BA14BEHS make the PVC softer. However, the $T_g(E''_{max}, 10\,Hz) = 71$ °C of the 10% BA14BEHS-blended PVC film is higher than $T_g(E''_{max}, 10\,Hz) = 56$ °C of the 10% DEHP-blended film, indicating that the plasticizing effectiveness of BA14BEHS is lower than that of DEHP. The $T_g(E''_{max}, 10\,Hz)$-values of the BA14BES-blended films were not shifted after aging for 48 h at 90 °C, suggesting again good compatibility of BA14BEHS with PVC resin.

No liquid material leached out leaching was observed visually form the 40% BA14BEHS-blended PVC film. However, the E' curve decreased slightly from around −40 °C and remarkably from around 50 °C, and the E'' curve gave two peaks at around −22 and 54 °C. The lower peak top temperature is close to the T_g of BA14BEHS, indicating that BA14BEHS was not fully miscible with PVC at the content.

Table 1. Glass Transition Temperature of the PVC Film Blended with BA14BEHS at Different Concentration

	0%	5%	10%	20%
$T_g(E''_{max}, 10\,Hz)$/°C	82	75	71	68

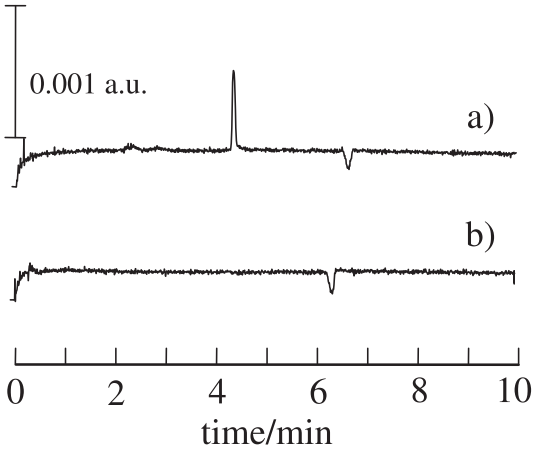

Figure 4. Electropherograms of a) 0.10 mM BA14BEHS in the 10 mM CH_3COOH, 10 mM CH_3COONa (1:1 W–AN) and b) the sample W–AN medium obtained when the 10% BA14BEHS-blended PVC film was contacted with water at room temperature for 7 days.

The $BA14^+$ salt with bis(2-ethylhexyl) phosphate ($BEHP^-$) anion maintains also its liquid state even at room temperature.[7] However, in contrast to the BA14BEHS-blended film, leaching was observed visually at the surfaces of the 10% BA14BEHP-blended PVC film. Although it has been reported that 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$) can be used as plasticizer for PVC,[6] leaching was observed visually at the surface of 10% $BMImPF_6$-blended PVC film. The results suggest that the compatibility of BA14BEHS with PVC is attributed chiefly to a strong interaction of the polar PVC molecule with the $BEHS^-$ anion like that with DEHP.

Leachability. Curve a in Figure 4 shows the electropherogram (absorbance vs. time curve) of 0.10 mM BA14BEHS in 10 mM CH_3COOH, 10 mM CH_3COONa (1:1 W–AN). A sharp peak was observed at the elution time of 4.3 min. The peak can be identified as $BA14^+$ cation based on the elution time of that of BA14Cl. The peak area was proportional to the concentration of BA14BEHS in the electrophoresis sample solution, and the detection limit was estimated to be 2 µM at a signal-to-noise ratio of 3.

Curve b in Figure 4 shows the electropherogram of the sample W–AN medium obtained when the 10% BA14BEHS-blended PVC film was in contact with water at room temperature for 7 days. The BA14BEHS was not detected in the sample W–AN medium, so that the leaching level of BA14BEHS was estimated to be less than 1 $\mu g\,cm^{-2}$ from the detection limit. The leaching of BA14BEHS was not detected also when the PVC film was in contact with water for 1 h at 90 °C, which is higher than the $T_g(E''_{max}, 10\,Hz)$ of the film. Similarly, no leaching of BA14BEHS was detected when the film was in contact with heptane at room temperature for 1 day.

Table 2. Leaching Levels (in μg cm^{-2}) of the Additives Tested from the PVC Film

Additives	Water		Heptane
	Room temp 7 days	90 °C 1 h	Room temp 1 day
10% BA14BEHS	n.d.[a]	n.d.	n.d.
40% BA14BEHS	n.d.	n.d.	35 ± 2
5% BA14BEHP	3 ± 1	3 ± 1	3 ± 1
10% DEHP	n.d.	n.d.	n.d.
10% BMImPF6	89 ± 4	23 ± 3	n.d.

a) n.d.: <1 μg cm^{-2}.

Leaching was not detected when the 40% BA14BEHS-blended PVC film was in contact with water, but the leaching level was determined to be 35 ± 2 μg cm^{-2} when the film was in contact with heptane as shown in Table 2. The amount of BA14BEHS leached out corresponds to 1% of the BA14BEHS initially present in the PVC film. This may be attributed to the fact that BA14BEHS at 40% content was not miscible fully with PVC resin.

The leaching level when 5% BA14BEHP-blended PVC film was in contact with water and heptane under these conditions was determined to be 3 ± 1 μg cm^{-2}, indicating again that BA14BEHP was not well compatible with PVC. Similarly, the leaching levels of $BMImPF_6$ from the 10% $BMImPF_6$-blended PVC were 89 ± 4 and 23 ± 3 μg cm^{-2} when the film was in contact with water at room temperature for 7 days and at 90 °C for 1 h, respectively. The leaching level of DEHP to water from PVC groves is reported as 0.01–0.1 μg cm^{-2} levels at 60 and 95 °C for 30 min.[18] However, in this experiment no leaching of DEHP was detected from the 10% DEHP-blended PVC. A more sensitive technique should be needed for the comparison of the leachability of BA14BEHS with DEHP.

Surface Resistivity. Cationic surfactants including BA14Cl are used as antistatic additives for polymers.[19] They migrate to the surface of the polymer to form a uniform layer of their hydrophilic part, which absorbs humidity to form a conductive pass of a thin water layer. However, the surface resistivity of the 10% BA14BEHS-blended PVC film at 20 °C and 40% relative humidity was more than 2×10^{13} ohms. The 10% DEHP-blended PVC film also gave resistivity of more than 2×10^{13} ohms. The BA14BEHP is leachable from the PVC film as mentioned above, and the $BEHP^-$ anion can be hydrated.[7] The PVC film blended with both 5% BA14BEHP and 5% BA14BEHS gave a lower surface resistivity of 1×10^{12} ohms. The results indicate that BA14BEHS cannot act like conventional cationic surfactants in PVC. This may be related also to the antimicrobial action discussed below.

Antimicrobial Test. The antimicrobial test for the PVC film without additives, which is used as a control, gave $N_{std} = 8000$–17000 CFU per agar plate in six experiments. The antimicrobial performance of BA14BEHS, BA14EHP, DEHP as PVC additives was estimated as $(\log[N_{std}] - \log[N])$ with the number of colonies N obtained for the sample films. The 95% confidence level for the average of $(\log[N_{std}] - \log[N])$ ($n = 6$) are listed in Table 3. The 10% DEHP-blended PVC film gave $(\log[N_{std}] - \log[N]) = 0.0 \pm 0.3$, and therefore DEHP can be considered to be antimicrobially inactive. The 5% BA14BEHP-blended PVC film gave $(\log[N_{std}] - \log[N]) = 1.7 \pm 1.0$. If BA14BEHP is assumed to leach out to the test bacterial suspension (50 μL) from the interfacial area of 1 cm^2 at 3 μg cm^{-2} level, the amount of BA14BEHP in the bacterial suspension can be estimated to be 60 ppm, which is comparable to the minimum inhibitory concentration for the BA14BEHP emulsion (50 ppm).[7] Thus the antimicrobial effect of the 5% BA14BEHP-blended PVC film may be attributed to the release of BA14BEHP.

Table 3. Antimicrobial Activities $(\log[N_{std}] - \log[N])$ of the PVC Films against *E. coli* JM 109

Additives	$\log[N_{std}] - \log[N]$
5% BA14BEHS	>4.0
5% BA14BEHP	1.7 ± 1.0
5% BA14BEHS + 5% BA14BEHP	1.2 ± 1.0
5% DEHP	0.0 ± 0.3

Interestingly, in the antimicrobial test for the 5% BA14BEHS-blended PVC film, bacterial cells were hardly observed in the agar plate, and $(\log[N_{std}] - \log[N])$ was estimated to be more than 4.0. Since the leaching level of BA14BEHS is less than that of BA14BEHP and the BA14BEHS emulsion did not kill *E. coli* JM109 even at 1000 ppm,[7] the antimicrobial effect of the PVC film cannot be explained by the release of BA14BEHS. It has been known that surface-bonded organosilicon quaternary ammoniums show strong antimicrobial activity without release of the agents.[20,21] Similarly to the immobilized antimicrobial agents, it is postulated that the antimicrobial effect may be due to disruption of membrane function with possible cell lysis caused by the high concentration of $BA14^+$ cation on the film surface. The PVC film blended with both 5% BA14BEHS and 5% BA14BEHP gave $(\log[N_{std}] - \log[N]) = 1.2 \pm 1.0$, which is lower than those with 5% BA14BEHS or BA14BEHP only. The antimicrobial additives may affect the mode of action each other. Now the study is being extended to other bacteria.

Conclusion

The BA14BEHS is a halogen-free low-volatile liquid material. The BA14BEHS showed good compatibility with PVC resin. The BA14BEHS-blended PVC film exhibited low-leachability of BA14BEHS. Thus, the BA14BEHS is interesting as a plasticizer for PVC. The BA14BEHS-blended film exhibited antimicrobial performance against *E. coli* JM 109. The use of BA14BEHS as antimicrobial agent for PVC is also interesting.

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References

1 B. Weyershausen, K. Lehmann, *Green Chem.* **2005**, *7*, 15.

2 P. L. Short, *Ionic Liquids*, in *Chem. Eng. News* **2006**, *84*, April 24, 15.

3 W. L. Hough, R. D. Rogers, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2262.

4 M. P. Scott, C. S. Brazel, M. G. Benton, J. W. Mays, J. D.

Holbrey, R. D. Rogers, *Chem. Commun.* **2002**, 1370.

5 M. P. Scott, M. Rahman, C. S. Brazel, *Eur. Polym. J.* **2003**, *39*, 1947.

6 M. Rahman, C. B. Brazel, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2004**, *45*, 301.

7 H. Katano, M. Akita, H. Tatsumi, T. Tsukatani, *J. Antibact. Antifungal Agents* **2007**, *35*, 147.

8 R. S. Shelton, M. G. van Campen, C. H. Tilford, H. C. Lang, L. Nisonger, F. J. Bandelin, H. L. Rubenkoenig, *J. Am. Chem. Soc.* **1946**, *68*, 753.

9 K. Jono, T. Takayama, M. Kuno, E. Higashide, *Chem. Pharm. Bull.* **1986**, *34*, 4215.

10 K. Heinig, C. Vogt, G. Werner, *Fresenius' J. Anal. Chem.* **1997**, *358*, 500.

11 Japanese Industrial Standard JIS Z2801: 200 (E).

12 J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed., **1986**, Wiley.

13 S. Mitsunobu, Y. Takahashi, *Water, Air, Soil Pollut.* **2006**, *175*, 99.

14 M. Galiński, A. Lewandowski, I. Stępniak, *Electrochim. Acta* **2006**, *51*, 5567.

15 H. Matsumoto, H. Kageyama, Y. Miyazaki, *Chem. Lett.* **2001**, 182.

16 T. Makino, *J. Soc. Mater. Sci., Jpn.* **2005**, *54*, 221.

17 K. Schmieder, K. Wolf, *Kolloid. Z.* **1952**, *127*, 65.

18 Y. Kawamura, T. Maehara, C. Wakui, T. Yamada, *Shokuhin Eiseigaku Zasshi* **2000**, *41*, 330.

19 *Plastics Additives Handbook*, 5th ed., ed. by H. Zweifel, Hanser Publications, **2001**.

20 P. A. Walters, E. A. Abbott, A. J. Isquith, *Appl. Microbiol.* **1973**, *25*, 253.

21 H. Kourai, K. Nakagawa, *J. Antibact. Antifungal Agents* **1991**, *19*, 53.