Novel Linear and Cross-Linked Acrylate Polymers Bearing *O*-Cyanoethylated (Glycosyloxy)ethyl Side Chain with High Dielectric Properties over Wide Temperature Range

Ryosuke Nishida, Teruhiko Ishikawa, and Seiki Saito*
Department of Bioscience and Biotechnology, Faculty of Engineering, Okayama University, Tsushima, Okayama 700-8530

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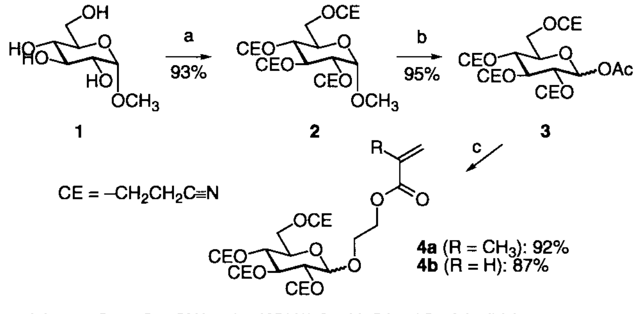
UV-irradiation (365 nm) on a spreaded mixture of 2-[tetra-*O*-(cyanoethyl)glucopyranosyloxy]ethyl acrylate and ethylene glycol dimethacrylate onto a copper plate gave a cross-linked copolymer which exhibited extremely stable and high dielectric permittivity (ε') of 23 to 30 (–100 to –10 °C) and as high as 49 even at 20 °C.

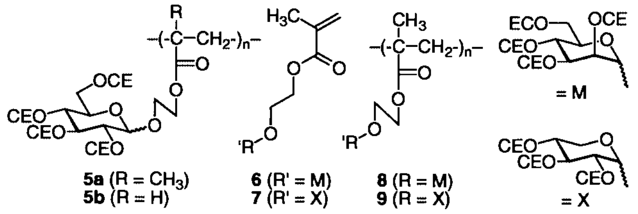
Polymers with high dielectric properties are practically used as electronic devices such as binders of electro-luminescence lamps, condensers, etc.[1–3] Hence, much better dielectric properties of polymers are demanded in order to meet recent requirements such as higher function, higher ability, and miniaturization. At present *O*-cyanoethylated polysaccharides derived from cellulose or pullulan, etc.[4] are playing an important role as a leading material for such a purpose, and Michael-type cyanoethylation reaction is employed as a key step in which acrylonitrile is used as the Michael acceptor. However, this process is hard to proceed quantitatively, and the considerable portion of hydroxy groups remained intact in these polymers, which is responsible for moisture absorption, and thus is harmful to their practical performance.[5]

This situation turned our attention to the preparation of fully *O*-cyanoethylated 2-(glycosyloxy)ethyl acrylate monomers (**4**) and its polymerization to provide high dielectric acrylate polymers (**5**) with a cyanoethylated glycoside-bearing side chain in which no free hydroxy group remains. A synthetic route to **4** starting from methyl glycosides (**1**) of natural monosaccharides has been established as delineated below in the case of D-glucose.[6] It turned out that this method was applicable to D-mannose and D-xylose, and the corresponding methacrylate monomers (**6**, **7**) were furnished uneventfully.



(a) 50 × CH_2=CH-CN/0.06 × KOH/0.3 × H_2O/50 °C,18 h; (b) large excess Ac_2O/0.3 × H_2SO_4/25 °C, 0.5 h; (c) 2-hydroxyethyl methacrylate (HEMA) or 2-hydroxyethyl acrylate (HEA)/0.2 ×TMSOTf/50 °C, 1 h.

The bulk polymerization of **4a** was effected by using 2,2'-azobis(2,4-dimethylvaleronitrile) (AVN) as an initiator at 65 °C for 3 days under nitrogen to give the corresponding polymer **5a** (98% conversion) with molecular weight (M_w) of 234000 (M_w/M_n = 4.7).[7] In addition, mannose and xylose-based methacrylate polymers **8** and **9** were obtained respectively from **6** and **7** prepared via a series of reactions shown above. Their physical properties such as M_w, M_w/M_n, T_g,[8] dielectric permittivity (ε'), dielectric loss (ε''), and activation energy for β-relaxation (E_β)[9] were determined in a standard manner, which were summarized in Table 1.



5a (R = CH_3)
5b (R = H)

6 (R' = M)
7 (R' = X)

8 (R = M)
9 (R = X)

Table 1. Physical properties of *O*-cyanoethylated 2-(glycosyloxy)ethyl methacrylate polymers **5a**, **8**, and **9**

Polymer	$M_w{}^a/10^5$	M_w/M_n	$T_g{}^b$/°C	ε'^c	ε''^c	$E_\beta{}^d$/kJ·mol^{-1}
5a	2.34	4.74	30	20	0.1	72
8	2.30	3.17	23	34	1.2	94
9	–[e]	–[e]	29	28	0.78	66

[a]Determined by gel permeation chromatography. [b]Determined by differential scanning calorimetry. [c]At 20 °C and 1000 Hz. [d]Obtained from Arrhenius plots of f_{max} available through the frequency dependence of dielectric loss (ε'') at various temperatures. [e]Not determined because of the very low solubility of **9** even in DMF.

In Figure 1 are illustrated the temperature dependences of ε' and ε'' for **5a**, **8**, and **9**. The patterns of temperature dependence curves for these methacrylate polymers were quite similar to each other. Each polymer exhibited generally higher ε'-values even at low temperature than *O*-cyanoethylated natural polysaccharides such as pullulan, dextran, or amylose.[3,4]

A much more interesting dielectric feature was observed for cross-linked copolymers (**10**) obtained from *O*-cyanoethylated 2-(glucopyranosyloxy)ethyl acrylate **4b** and ethylene glycol dimethacrylate (EGDMA). A mixture of **4b** and EGDMA in a ratio 9/1 or 7/3 containing benzil mono-dimethylacetal (4%) was spreaded onto a copper plate and irradiated with a UV lamp (365 nm) at 50 °C for 30 min. The resulting film could not be dissolved in any solvent, supporting the successful formation of cross-linked polymer **10**, the dielectric properties of which were measured and illustrated in Figure 2.

These polymers exhibited ε'-values of 23 (**10**$_{(9/1)}$) and as high as 49 ($\mathbf{10}_{(7/3)}$) at 20 °C (1000 Hz). In particular, ε' = 49 (20 °C) is the highest value among those observed so far for cyanoethylated natural polysaccharides or artificial vinyl polymers,[3,4] although an exact reason why $\mathbf{10}_{(7/3)}$ with a low content of the cyanoethyl group has higher ε' is not clear. In addition **10** exhibited very stable and almost constant value of $\varepsilon' \cong 25$ over the temperature range of –100 to –10 °C (Figure 2) in marked contrast to the linear polymers **5a**, **8**, and **9** (Figure 1). The low temperature maximum of ε'' around –50 °C that was typical for the linear polymers almost disappeared for **10**. This is probably because random molecular orientation is kept by photo-induced crosslinking in the case of **10**.

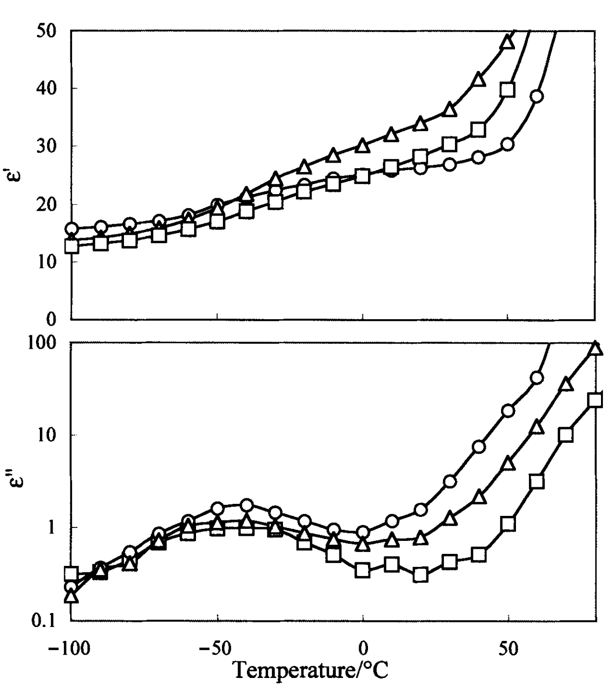


Figure 1. Temperature dependences of ε' and ε" at 1000 Hz for polymers **5a** (○), **8** (△), and **9** (□).

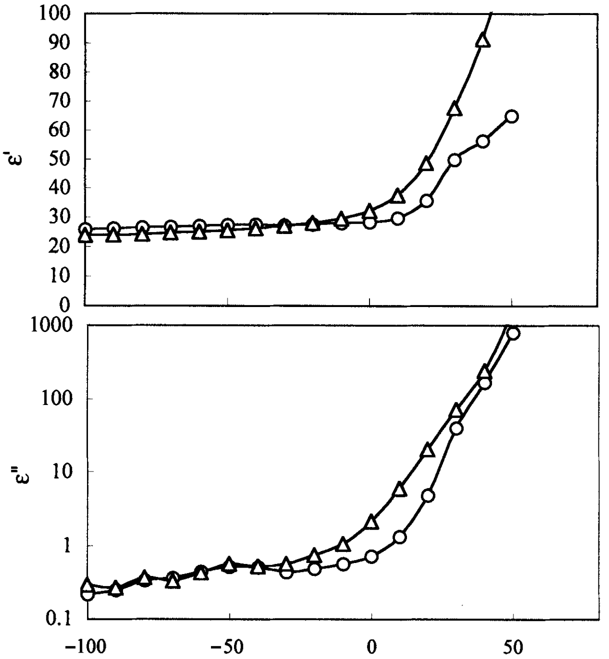
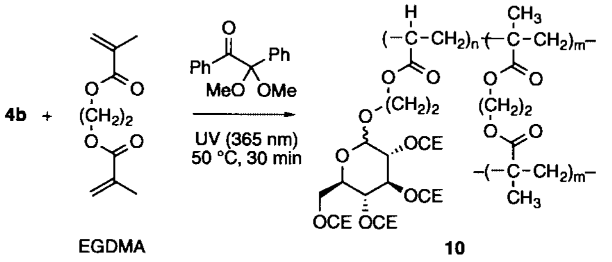


Figure 2. Temperature dependences of ε' and ε" at 1000 Hz for **10**: **4b**/ EGDMA ratio = 9/1 (○), 7/3 (△).



In any event, an easy access to monomers such as **4** provides considerable advantages and opportunities for developing novel high dielectric polymers as delineated in this work. We are now making efforts, relying on such chemistry, to find materials in this currently developing field.

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References and Notes

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6 The details of this synthesis will be reported elsewhere.
7 The polymer **5a** could be stored on a shelf for several months without any appreciable change in the dielectric constant (ε') and, in addition, its TG–DTA analysis proved no weight loss up to 250 °C.
8 The values of T_g were generally higher than those observed for the previous *O*-cyanoethylated vinylic polymers: see a) A. B. Bedekar, Y. Tsujii, N. Ide, Y. Kita, T. Fukuda, and T. Miyamoto, *Polymer*, **36**, 4735 (1995). b) S. Yamaguchi, S. Tasaka, and N. Inagaki, *Polymer Preprints, Japan*, **39**, 3710 (1990).
9 The similar value for the β-activation was previously observed: see Y. Nakayama, N. Kohara, and H. Toyota, *J. Soc. Fiber Sci. Technol., Jpn*, **51**, 200 (1995).