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ORIGINAL PAPER

Synthesis of well-defined norbornene–lactone-functionalized polymers via ATRP

Takuma Miyazaki · Boyong Xue · Kazufumi Kohno · Etsuo Hasegawa · Shigeyuki Iwasa · Akinori Toyota

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Abstract Well-defined norbornene–lactone-functionalized polymers were synthesized by atom transfer radical polymerization (ATRP) of 5-methacryloxy-6-hydroxynorbornene-2-carboxylic-6-lactone (MNL) and 5-acryloxy-6-hydroxynorbornene-2-carboxylic-6-lactone (ANL) monomers. The ATRP of MNL initiated by ethyl 2-bromopropionate (EBrP), in both *N*,*N*-dimethylformamide (DMF) and *o*-dichlorobenzene (ODCB) solvents was successfully carried out in the presence of CuCl/CuBr and *N,N,N″,N″,N″*-pentamethyltriethylenetetramine (PMDETA) at 70 °C. The CuCl/ODCB catalyst system gave rise to a lower M_w/M_n ($\leqq 1.20$) than CuBr/DMF catalyst system. The ATRP of ANL was feasible in the presence of CuBr and PMDETA at 70 °C but showed lower reactivity than MNL. The resulting polymers were characterized by means of gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy.

Keywords Atom transfer radical polymerization · Norbornene · Lactone · Living radical polymerization · Dry-etching resistance · Positive resist

Introduction

To satisfy advanced semiconductor lithography, lactone-units polymer has been proposed and used as an ArF excimer laser ($\lambda = 193.4$ nm) chemically amplified positive resist [1–4]. In general, 193 nm single-layer resists require three basic

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T. Miyazaki · B. Xue · K. Kohno · A. Toyota (✉)
Graduate School of Engineering, Tokyo University of Agriculture and Technology,
2-24-16 Naka-cho Koganei-shi, Tokyo 184-8588, Japan
e-mail: a-toyota@cc.tuat.ac.jp

E. Hasegawa · S. Iwasa
Nano Electronics Research Laboratories, NEC Corporation, Tokyo, Japan

properties: high optical transparency at 193 nm, good dry-etch resistance, and thermal stability to withstand the temperature and process conditions used in device manufacturing [3, 5, 6]. After the identification of the effect of alicyclic moieties on dry-etch resistance, outstanding achievement has been reported [5–9]. The acrylate polymers bearing alicyclic units, adamantyl and isobornyl groups show excellent lithographic capability due to the fact that etching durability of polymer materials is derived from their high carbon contents [10]. However, due to the absence of hydrophilic substituents, the above acrylate polymers should be modified with a hydrophilic acrylate derivative to enhance their adhesion and solubility properties via copolymerization [3, 11]. To combine two function of etch resistance and adhesion, acrylate monomers bearing single plane cyclic lactone ester structure such as mevalonic lactone and γ-butyrolactone were used to prepare the single-layer resist material [5]. Unfortunately, the etch-resistance ability resulted from plane cyclic lactone groups was deficient. Last decade, norbornene–lactone was proposed initiatively as an effective group to satisfy comprehensive requirement [2, 11]. Subsequently, oxatricyclodecaneone [12] and adamantine–lactone [13] structures have proved high efficient to enhance etch resistance. Herein, norbornene–lactone has been utilized due to the low cost, simple synthesis process and high thermal stability. Two representative acrylate norbornene–lactone monomers are 5-acryloxy-6-hydroxynorbornane-2-carboxylic-6-lactone (ANL) and 5-methacryloxy-6-hydroxynorbornane-2-carboxylic-6-lactone (MNL).

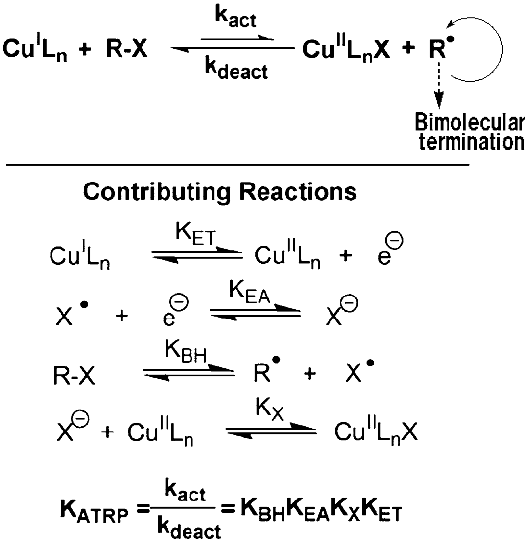
Our interest in the development of 193 nm single-layer resists materials based on norbornene–lactone derivatives and atom transfer radical polymerization (ATRP) strategies led us to synthesis a series of novel polymers bearing norbornene–lactone recently. ATRP is a versatile method in the synthesis of polymers with controllable molecular weight and low molecular-weight distribution. Furthermore, a polymer can be endowed with multifunction and varied morphological structure via ATRP copolymerization [14–16]. It is proposed that the overall atom transfer equilibrium can be viewed as a combination of four reversible reactions [17] as shown in Scheme 1. On the basis of this theory, we chose adaptable catalyst/ligand system, and realized ATRP of ANL and MNL primarily. The effect of catalyst and solvent on polymerization behavior was investigated. The results could be expected as a good reference for the following research on precise copolymerization of MNL/ANL and other comonomer. To the best of our knowledge, there are so far no reports on ATRP of MNL and ANL. Here we report the first preparation of a well-defined homopolymer of MNL and ANL using ATRP.

Experimental

Materials

Monomers 5-methacryloxy-6-hydroxynorbornene-2-carboxylic-6-lactone (MNL) and 5-acryloxy-6-hydroxynorbornene-2-carboxylic-6-lactone (ANL) were provided by NEC Corporation; *N,N,N″,N″,N″*-pentamethyltriethylenetetramine (PMDETA) was available from Aldrich and used as received. Copper (I) chloride (CuCl) was

Scheme 1 Proposed atom transfer equilibrium mechanism [15]



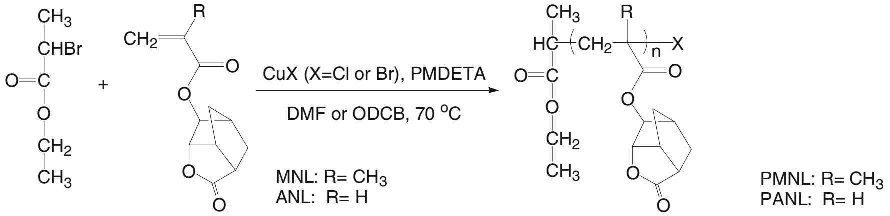
available from WAKO and copper (I) bromide (CuBr) was available from Aldrich. Ethyl 2-bromopropionate (EBrP) was used as received from WAKO. *N*,*N*-dimethylformamide (DMF) and *o*-dichlorobenzene (ODCB) were purchased from KANTO CHEMICAL and were dried by standard methods before use.

Measurements

^{1}H NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer. The number average molecular weights (M_n) and polydispersity index (M_w/M_n) of the polymers were determined with a JASCO gel permeation chromatography (GPC) equipped with a Shodex K-805L chromatograph column and a JASCO RI-2031 detector, using chloroform as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C.

Polymerization

In a typical experiment (Scheme 2), a 10 mL glass tube with a magnetic stirrer was charged with MNL (885.0 mg, 4.0 mmol), EBrP (7.2 mg, 0.04 mmol), CuBr (5.8 mg, 0.04 mmol), PMDETA (27.7 mg, 0.16 mmol), and DMF (4 mL). After degassing with five freeze–pump–thaw cycles, the polymerization tube was sealed under vacuum and placed into an oil bath at 70 °C. After 30 min, the mixture was cooled down to room temperature, and the tube was opened. The polymer solution in DMF was poured into an excess of methanol. The precipitate was collected by filtration, and dried in vacuum for 6 h at 40 °C to yield 732.6 mg PMNL as a white solid. The conversion was determined by gravimetry. PMNL ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 4.35–4.75 (m, 2H, OCHCHO of the norbornene–lactone ring), 3.16–3.28 (m, 1H, CHCOO), 2.40–2.70 (m, 4H, $2\times CH_2CHCOO$ of the norbornene–lactone ring). PANL ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 4.35–4.65 (m, 2H, OCHCHO



Scheme 2 ATRP of norbornene–lactone monomers MNL and ANL

of the norbornene–lactone ring), 4.05–4.14 (t, 1H, α-CH-Br), 3.15–3.33 (m, 1H, CHCOO of the norbornene–lactone ring), 2.40–2.70 (m, 4H, 2×CH_2CHCOO of the norbornene–lactone ring).

Results and discussion

Polymerization of MNL

ATRP of MNL was carried out in DMF and ODCB solvent at 70 °C by using 1 M equivalent of EBrP as initiator, 1 M equivalent of Cu (I) as catalyst, and 4 M equivalent of PMDETA as ligand ([M]: [I]: [Cu]: [L] = 100:1:1:4). Herein, two kinds of Cu (I) catalyst were used to investigate the effect of catalyst. The results were shown in Table 1. It should be evidently found that the molecular weight obtained during the polymerization increased linearly with monomer conversion and close to the theoretical number average molecular weight $M_{n(th)}$ when polymerization was catalyzed by CuCl (Fig. 1), and the resulting PMNLs possessed a narrow molecular weight distribution (M_w/M_n = 1.19–1.35). In the case of Run 1–4, the reactivity was so high that the polymerization process showed less

Table 1 ATRP results of MNL in DMF

Run	Cu(I)	Time (min)	Conv. (%)	M_n^a (/10^3)	M_w/M_n^a	$M_{n(th)}$ (/10^3)^b
1	CuBr	10	37.3	10.9	1.54	8.4
2	CuBr	30	49.1	12.7	1.69	11.0
3	CuBr	90	67.3	13.0	1.61	15.1
4	CuBr	360	76.1	14.2	1.59	17.0
5	CuCl	10	5.6	4.0	1.19	1.4
6	CuCl	60	26.1	6.2	1.28	5.9
7	CuCl	90	31.3	7.5	1.26	7.1
8	CuCl	360	82.7	15.4	1.35	18.5

Polymerization conditions: DMF = 4.0 mL, MNL = 4.0 mmol, EBrP = 0.04 mmol, Cu(I) = 0.04 mmol, PMDETA = 0.16 mmol, [M]: [I]: [Cu]: [L] = 100:1:1:4, 70 °C

[a] Determined by GPC calibrated by polystyrene standards at 40 °C

[b] Theoretical values

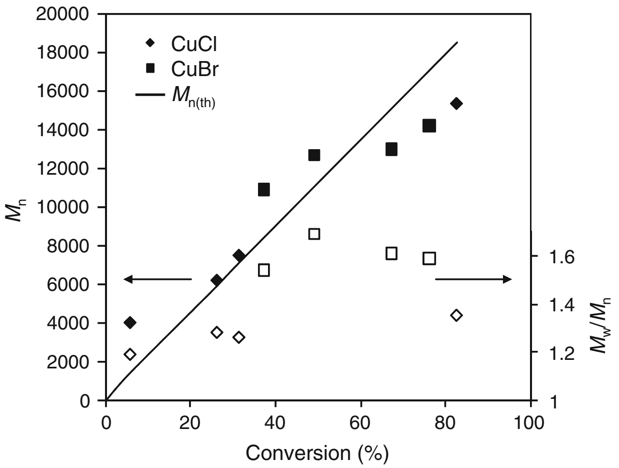


Fig. 1 Dependence of the molecular weight and molecular weight distribution on the conversion of MNL. [M]: [I]: [Cu]: [L] = 100:1:1:4; $T = 70$ °C, in DMF

controllability when polymerization of MNL was catalyzed by CuBr. Consequently, the resulting PMNLs had a broad molecular weight distribution ($M_w/M_n = 1.54 \sim 1.69$). These results indicate that CuBr catalyst gives rise to a high reaction speed, while CuCl catalyst gives rise to a well controllability for ATRP of MNL with the same complex. As shown in Scheme 1, this phenomenon should be attributed to a fact that the bond dissociation energy of the C–Cl bond is higher than that of C–Br bond [17, 18].

ATRP of MNL was carried out in ODCB, the polymerization showed a better controllability than above two reaction systems. The results were shown in Table 2 and Fig. 2. The M_n of the resulting PMNLs also increased linearly with increasing monomer conversion. The molecular weight distributions were narrower ($M_w/M_n = 1.14$–1.20) than those in above two cases. The kinetic plots of ATRP of MNLs in DMF and ODCB solvents were shown in Fig. 3. The first order linear

Table 2 ATRP results of MNL in ODCB

Run	Cu(I)	Time (min)	Conv. (%)	M_n^a (/10^3)	M_w/M_n^a	$M_{n(th)}$ (/10^3)^b
9	CuCl	30	29.9	8.6	1.14	6.8
10	CuCl	120	59.0	10.8	1.16	13.2
11	CuCl	240	70.7	14.6	1.20	15.8
12	CuCl	360	87.4	17.5	1.15	19.5

Polymerization conditions: ODCB = 4.0 mL, MNL = 4.0 mmol, EBrP = 0.04 mmol

Cu(I) = 0.04 mmol, PMDETA = 0.16 mmol, [M]: [I]: [Cu]: [L] = 100:1:1:4, 70 °C

[a] Determined by GPC calibrated by polystyrene standards at 40 °C

[b] Theoretical values

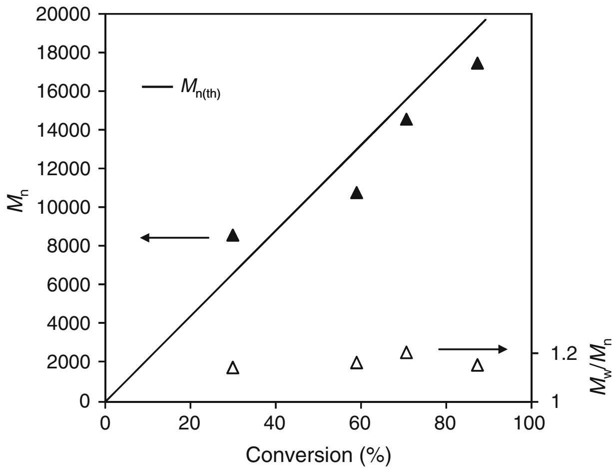


Fig. 2 Dependence of the molecular weight and molecular weight distribution on the conversion of MNL. [M]: [I]: [Cu]: [L] = 100:1:1:4; $T = 70$ °C, in ODCB

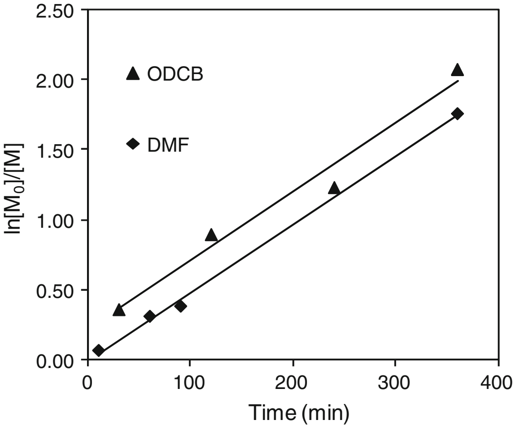
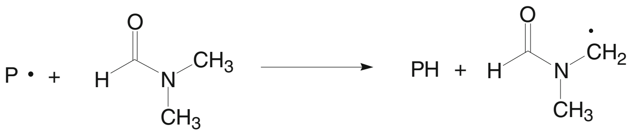


Fig. 3 Kinetic plot of the polymerization of MNL in different solvents (where $[M]_0$ is the initial monomer concentration and [M] is the monomer concentration at different time)

dependence of $\ln([M]_0/[M])$ versus the polymerization time indicated that the radical concentration remained constant throughout the polymerization. After calculation of apparent rate constant of propagation ($k_p^{app}{}_{MNL}$) from slope, it was found that both of them were nearly 8.16×10^{-5} s^{-1}. Therefore, it can be concluded that the ATRP of MNL in DMF or ODCB solvent has a similar polymerization rate with the same catalyst and ligand. However, they have obvious difference at the beginning of the reaction. In the case of DMF, the reaction had a longer induction period (approximately 3 min determined with kinetic plot Fig. 3). This phenomenon may be due to the high chain transfer property of DMF solvent. During the formation of the actual initiating center resulting from the interaction between the initiator and the catalyst, the radical transfers to DMF solvent and postpones the establishment of equilibrium (Scheme 3).



Scheme 3 Proposed mechanistic radical transfer to DMF solvent

Polymerization of ANL

In fact, the same process was attempted to polymerize ANL by using CuCl as catalyst. Unfortunately, the polymerization was infeasible due to the higher bond dissociation energy of the C–Cl bond. Alternatively, ATRP of ANL was carried out in DMF at 70 °C by using 1 M equivalent of EBrP as initiator, 1 M equivalent of CuBr as catalyst, and 4 M equivalent of PMDETA as ligand ([M]: [I]: [Cu]: [L] = 100:1:1:4). The results were shown in Table 3. The molecular weight of the resulting PANL increased linearly with monomer conversion and closed to the theoretical values up to 38.8% conversion. After this point, it was difficult to get a higher conversion, even though polymerization time was prolonged. The molecular weight distribution was narrow ($M_w/M_n = 1.08–1.31$). The kinetic plot of ATRP of ANL in DMF was shown in Fig. 4. The first order linear dependence of $\ln([M]_0/[M])$ versus the polymerization time indicates that the radical concentration remains constant throughout the polymerization. The apparent rate constant of propagation ($k_p^{app}{}_{ANL} = 3.9 \times 10^{-6}\ s^{-1}$) was calculated from slope. Compared with ATRP of MNL with CuBr under the same polymerization condition, it was evidently found that ANL showed lower reactivity than MNL. This could be attributed to the effect of substitution [19, 20]. For different alkyl halides, the value of K_{ATRP} depends upon the degree of substitution (primary < secondary). Therefore, methyl in acryl of MNL was a radical-stabilizing group, and then resulted in a higher reactivity.

Conclusions

ATRP of MNL and ANL monomers was applied to synthesis norbornene–lactone-functionalized polymers with a controllable molecular weight and a narrow

Table 3 ATRP results of ANL in DMF with CuBr as catalyst

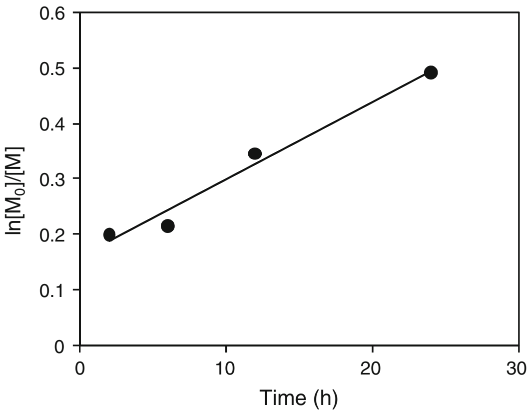
Run	Time (h)	Conv. (%)	M_n^a ($/10^3$)	M_w/M_n^a	$M_{n(th)}$ ($/10^3$)^b
13	2	18.1	3.5	1.08	3.7
14	6	19.3	4.1	1.12	4.0
15	12	29.2	5.2	1.31	6.1
16	24	38.8	6.2	1.22	8.0

Polymerization conditions: DMF = 4.0 mL, ANL = 4.0 mmol, EBrP = 0.04 mmol, CuBr = 0.04 mmol, PMDETA = 0.16 mmol, [M]: [I]: [Cu]: [L] = 100:1:1:4, 70 °C

[a] Determined by GPC calibrated by polystyrene standards at 40 °C

[b] Theoretical values

Fig. 4 Kinetic plot of the polymerization of ANL (where $[M]_0$ is the initial monomer concentration and [M] is the monomer concentration at different time)



molecular weight distribution. Ethyl 2-bromopropionate (EBrP) combined with CuCl/PMDETA catalyst system enables efficient control of the molecular weight over the whole polymerization. The ATRP of ANL was feasible only in the presence of CuBr and PMDETA at 70 °C. The results demonstrated that monomer MNL has higher reactivity than monomer ANL.

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