Evidence for Polarity- and Viscosity-Controlled Domains in the Termination Reaction in the Radical Polymerization of Acrylonitrile

Xiaopei Li,[1] *Tasuku Ogihara,*[1] *Tatsuhisa Kato,*[1] *Yasuyuki Nakamura,*[2,*] *and Shigeru Yamago*[1,*]

[1]Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan

[2]Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan

KEYWORDS: Radical polymerization, Termination mechanism, Viscosity, Polar effect, Acryronitrile, Radical coupling reaction

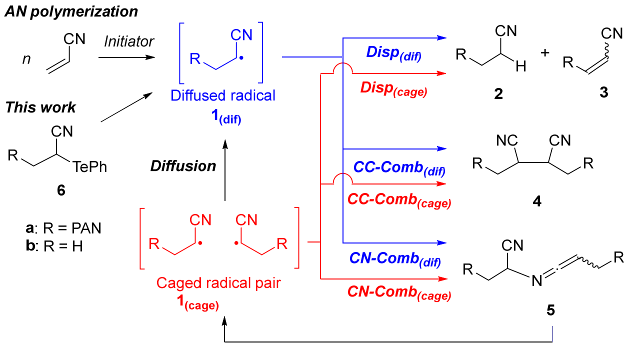
This paper is dedicated to Prof. Ilhyong Ryu of Osaka Prefectural University for his 70th birthday.

ABSTRACT: The termination mechanism in the radical polymerization of acrylonitrile (AN) was determined by the reaction of structurally well-defined polyacryronitrile (PAN) chain-end radical **1a** and PAN-end mimetic small model radical **1b**. The contributions of three mechanisms, i.e., the disproportionation (*Disp*), the combination by carbon-carbon formation (*CC-Comb*), and the combination by carbon-nitrogen bond formation (*CN-Comb*), were unambiguously determined. The *CN-Comb* pathway was experimentally proved for the first time. The selectivity between *Disp* and *CC-Comb* showed a good correlation with the viscosity and temperature, and the *Disp* selectivity increased as the viscosity increased, as previously reported for the termination of other monomers. In contrast, *CN-Comb* is insensitive to viscosity but sensitive to polarity; the selectivity decreases as the polarity of the media increases. The results strongly suggest the presence of two domains in the termination reaction, namely, the polarity- and viscosity-controlled domains. *CN-Comb* product **5** was stable under the polymerization conditions but decomposed to *Disp* and *CC-Comb* products at high temperatures. Therefore, care must be taken in the processing step, such as the molding process, because the physical properties could be altered due to changes in the *Disp* and *CC-Comb* compositions.

INTRODUCTION

Radical polymerization is the most important synthetic method for fabricating polymer materials industrially, but the mechanism of its important elementary step, i.e., the termination reaction giving dead polymers by either disproportionation (*Disp*) or combination (*Comb*), is still unclear and controversial (Scheme 1).[1, 2] The termination reaction determines the chain length and end-group structure of the polymer and further affects its properties, such as the toughness and thermal stability.[3, 4] Therefore, a clear understanding of the termination mechanism is an important issue for macromolecular engineering.

Polyacrylonitrile (PAN) is a commodity polymer prepared mainly by the radical polymerization of acrylonitrile (AN) and has various applications, such as in films, coatings, and fabrics.[5-10] PAN is also used as a precursor for fabricating high-quality carbon fibers, which are used for light-weight and high-strength structural materials such as body frames of airplanes and cars, and the properties of the fibers are influenced by the structure of the PAN.[11] Despite the practical importance of PAN, the termination mechanism in AN polymerization is still unclear to the best of our knowledge. The most striking feature in the AN termination is the presence of the combination mechanism by carbon-nitrogen bond formation (*CN-Comb*). Therefore, PAN radical **1a** (R = PAN) not only undergoes disproportionation (*Disp*), giving equal quantities of **2a** and **3a,** and combination by carbon-carbon bond formation (*CC-Comb*) to give **4a** but also proceeds through the *CN-Comb* pathway to give **5a** (Scheme 1). The termination of AN has already been studied by kinetic measurements, ^{14}C labeling experiments, and gelation methods, and all results supported the nearly complete *Comb* termination mechanism.[12-15] However, the contributions of *CC-* and *CN-Comb* were not clarified, and no experimental evidence has been reported to prove the occurrence of *CN-Comb* termination. Furthermore, factors controlling the termination mechanism were unclear.



Scheme 1. Termination reaction of a polymer chain end and its model radical related to AN polymerization.

Recently, we proposed a new protocol to clarify the termination mechanism based on product analysis by carrying out the reaction of structurally well-controlled polymer end radicals.[16-19] The precursor polymers were synthesized by organotellurim-mediated radical polymerization (TERP)[20-22] and were activated photochemically.[23-25] The generated radicals are diffused radicals that are free from the solvent cage effect[26, 27] and the analysis of molecular weights and polymer end group structures unambiguously quantify the contributions of *Disp* and *Comb*.

Here, we applied this method to clarify the termination mechanism in the radical polymerization of AN using diffused PAN-end radical **1a**$_{\mathbf{(dif)}}$ (R = PAN) and model radical **1b**$_{\mathbf{(dif)}}$ (R = H) generated from the corresponding organotellurium compounds **6a** and **6b**, respectively. The formation of *CN-Comb* products **5a** and **5b** was confirmed for the first time, and their thermal stability for regenerating **1** was also studied. The *Disp/CC-Comb* selectivity is sensitive to viscosity, particularly, microviscosity, as reported in the termination reaction of methacrylate and styrene polymerization.[19, 26, 28, 29] In contrast, the *CN-Comb* mechanism is insensitive to viscosity but is highly sensitive to the polarity of the reaction media, indicating that there are two domains controlling the termination, i.e., the polarity-controlled and viscosity-controlled domains. This is also the first example confirming the polarity effect in the termination reaction and clarifying the presence of two domains.

Note that the reaction rate constants giving *Disp* (k_d), *CC-Comb* (k_{CC}), *CN-Comb* (k_{CN}) should be considered for discussing termination selectivity. However, the selectivity characteristics of *Disp*, *CC-Comb*, and *CN-Comb* are used here because the termination takes place irreversibly so that the selectivity is identical to the relative rate constants.

EXPERIMENTAL SECTION

General procedures. Reactions were carried out under nitrogen atmosphere unless otherwise mentioned. In photoirradiation experiments, a 500 W high pressure mercury lamp (Ushio) was used as a light source with combinations of a cutoff filter (Asahi Techno Glass), and a white household 6 W LED (Panasonic) were used as light sources with combinations of a cutoff filter (Asahi Techno Glass) or a neutral density filter (Sigma Koki). The distance between the light source and a reaction vessel was set to be 10 cm. Viscosity of the reaction solution was measured with an electromagnetically spinning viscometer (EMS-1000, Kyoto Electronics Manufacturing) for the sample prepared under nitrogen atmosphere. Diffusion constant (*D*) was determined by the diffusion ordered spectroscopy (DOSY) NMR experiments (see below in details).

Materials. Unless otherwise noted, chemicals obtained from commercial suppliers were used as received. AN was washed with 5% aqueous NaOH solution to remove the stabilizer and was distilled over CaH_2. Hexane was distilled over CaH_2. CH_2Cl_2 was dried with P_2O_5 and distilled over anhydrous K_2CO_3. Acetone was distilled over anhydrous K_2CO_3. *N,N*-dimethylformamide (DMF) was dried over P_2O_5 and distilled after the removal of P_2O_5. Solvents were deoxygenated by bubbling nitrogen gas for over half an hour before use when necessary. 2-Bromopropanenitrile[30] and ethyl 2-(phenylltellanyl)isobutyrate.[31] was prepared following the reported procedures.

Characterization. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were measured with Varian Mercury Plus or Bruker Avance III for a $CDCl_3$, DMSO-d_6, C_6D_6, CD_3CN, or acetone-d_6 solution of a sample and are reported in ppm (δ) from internal tetramethylsilane or a solvent peak. High resolution mass spectra (HRMS) were obtained under fast atom-bombardment (FAB) condition or electron ionization (EI) condition. Size exclusion chromatography (SEC) was performed on a machine (Shodex GPC-101) equipped with two linearly connected polystyrene mixed gel columns at 40 °C using RI detector. DMF were used as an eluent with lithium bromide (0.010 mol L^{-1}). The SEC data were calibrated with PMMA standards. Hydrodynamic volume of polymers was measured using dynamic light scattering (DLS; ELSZ-1000ZS) at the backscattering angle of 165° at 25 °C. Electron Spin Resonance (ESR) spectra were measured with Bruker Elexsys E (X-band, 9.4 GHz). Infrared spectra are reported in cm^{-1}.

Synthesis of 2-(phenyltellanyl)propanenitrile (6b). Phenyllithium (15 mL, 1.10 M in cyclohexane and Et_2O, 16.5 mmol) was added slowly to a suspension of tellurium powder (2.1 g, 16.5 mmol) in THF (25 mL) at 0 °C, and the resulting solution was stirred at room temperature for 30 min. To this solution was added 2-bromopropanenitrile (2.2 g, 16.5 mmol) dropwisely at -40 °C, and the mixture was stirred at room temperature for 20 min. Deoxygenated water was added to the resulting mixture, and the aqueous phase was separated under a nitrogen atmosphere. The remaining organic phase was washed with deoxygenated saturated aqueous NH_4Cl solution, dried over $MgSO_4$, and filtered under nitrogen atmosphere. The solvent was removed under reduced pressure, and the residue was purified by a preparative gel permeation chromatography under nitrogen atmosphere to give the product (1.12 g, 47%). ^{1}H NMR ($CDCl_3$) 1.84 (d, J = 7.2 Hz, 3H), 3.72 (q, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H), ^{13}C NMR ($CDCl_3$) 5.9, 21.0, 110.7, 129.8, 141.1, HRMS (FAB) *m*/*z*: Calcd for $C_6H_8N_2$ $(M)^+$, 260.9797, found 260.9799, IR (KBr) 2225, 1571, 1473, 1435 cm^{-1}.

Synthesis of 6a. A solution of AN (3.8 mL, 58 mmol) and ethyl 2-(phenylltellanyl)isobutyrate (264 μL, 1.30 mmol) in deoxygenated ethylene carbonate (7.6 mL) was irradiated using a 6 W white LED lamp through a neutral density filter (20% transmittance) with stirring at 70 °C for 6 h. The conversion of the monomer (73%) was determined by ^{1}H NMR by taking an aliquot. The reaction mixture was dissolved in deoxygenated DMF and poured into vigorously stirred deoxygenated methanol under nitrogen atmosphere. The product was collected by a suction filtration and dried under reduced pressure to give **6a** (2.1 g, 62% yield). M_n (2400) and $Đ$ (1.10) were determined by SEC. The end-group fidelity (livingness) of **6a** was determined to be 95% by a chain extension experiment.

Synthesis of oligomer 6a for ESR measurement. A solution of methyl 2-(phenylltellanyl)isobutyrate (1.4 mL, 6.3 mmol) and AN (3.9 mL, 60 mmol) in C_6H_6 (4.9 mL) was irradiated using a 6 W white LED lamp through a neutral density filter (20% transmittance) with stirring at 70 °C for 1 h. The conversion of the monomer (29%) were determined by ^{1}H NMR by taking an aliquot. The remaining monomer and the solvent were removed under reduced pressure (1.2 torr at room temperature) to give oligomer **6a** (2.8 g, 27% yield). M_n (465) and *Đ* (1.20) were determined by ^{1}H NMR and mass spectroscopy, respectively.

ESR measurement of radical 1b. The ESR was measured for a solution of **6b** (7.7 mg, 0.025 mmol) in C_6D_6 (0.10 mL) under continuous irradiation with a 500 W Hg lamp through a 390 nm cutoff filter at 25 °C. The ESR resonated at $g = 2.00280$ as doublet of quartet of triplet with the hyperfine coupling constants of 2.281, 2.027, and 0.341 mT with hydrogens at α and β to the nitrile group and nitrogen atom, respectively (Figure 1a).[32]

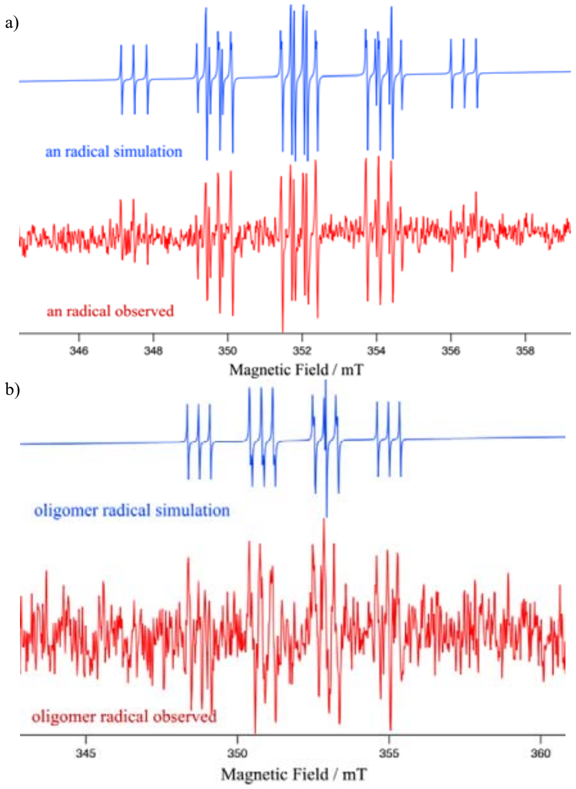


Figure 1. Simulated (blue) and experimental (red) ESR spectra of a) **1b** and b) **1a**.

ESR measurement of radical 1a. The measurement was done using oligomer of **6a** (11.6 mg, 0.025 mmol, M_n = 465, $Đ$ = 1.20) in C_6D_6 (0.10 mL), because **6a** having high molecular weight, even M_n = 2400, did not dissolve in benzene. The ESR was measured by continuous irradiation with a 500 W Hg lamp through a 390 nm cutoff filter at 25 °C. The ESR resonated at g = 2.00289 as doublet of triplet of triplet with the hyperfine coupling constants of 2.121, 2.071, and 0.379 mT with hydrogens at α and β to the nitrile group and nitrogen atom, respectively (Figure 1b).

The reaction of 6b and 2,2,6,6-tetramethylpyperidine 1-oxyl (TEMPO) under photo irradiation. A solution of **6b** (8.9 mg, 0.030 mmol) and TEMPO (5.1 mg, 0.033 mmol) in C_6D_6 (0.6 mL) was irradiated by a 500 W Hg lamp through a 470 nm cutoff filter at 25 ºC for 1.5 h under nitrogen atmosphere. The complete consumption of **6b** and the formation of TEMPO-adduct, 2-((2’,2’,6’,6’-tetramethylpiperidin-1-yl)oxy)propanenitrile, (100%) and diphenyl ditelluride (99%) were determined by the ^{1}H NMR analysis. ^{1}H NMR of the TEMPO adduct[33] (400 MHz; $CDCl_3$) 1.09 (s, 3H), 1.11 (s, 3H), 1.16 (s, 3H), 1.34(s, 3H),.1.31-1.36 (m, 1H), 1.47-1.50 (m, 5H), 1.55 (d, J = 7.0 Hz, 3H), 4.61 (q, J = 7.0 Hz, 1H).

Typical experimental procedure for the termination reaction starting from 6b. A solution of **6b** (8.9 mg, 0.030 mmol) in C_6D_6 (0.6 mL) was irradiated using a 500 W Hg lamp through a 390 nm cutoff filter at 60 ºC for 2 h. The consumption of **6b** (>99%) and the yields of termination products **2b**, **3b**, **4b** and **5b** (3%, 4%, 45% and 44%, respectively) were determined by ^{1}H NMR.

Isolation and characterization of 5b. A solution of **6b** (310 mg, 1.2 mmol) in hexane (30 mL) was irradiated through a 500 W high pressure Hg lamp through a 390 nm cutoff filter at 25 ºC for 2 h. After the consumption of **6b** monitored by ^{1}H NMR, the solvent was removed at rt under reduced pressure. The residue was distilled (10 °C, 10 torr) to afford **5b** as colorless oil (45 mg, 35% yield). ^{1}H NMR (DMSO-d$_6$) 1.46 (d, 3H), 1.59 (d, J = 7.2 Hz, 3H), 4.24 (br, 1H), 4.80 (br, 1H) (Figure 2a), ^{13}C NMR (CDCl$_3$) 8.3, 20.2, 48.5, 51.7, 118.0, 196.1, HRMS (EI) m/z: Calcd for $C_6H_8N_2$ (M + Na)$^+$, 131.0742, found 131.0713, IR (KBr) 2341 (C≡N), 2025 (C=C=N).

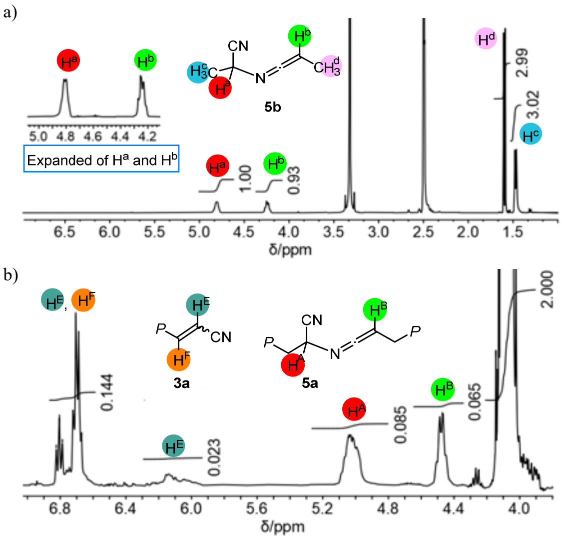


Figure 2. ^{1}H NMR spectra of a) isolated **5b** and b) partial ^{1}H NMR spectra of the reaction mixture obtained by the photolysis of **6a** in DMSO-d$_6$.

Typical experimental procedure for the termination reaction starting from 6a. A solution of **6a** (M_n = 2400, $Đ$ = 1.10, 120 mg, 0.030 mmol) in DMF (0.60 mL) was irradiated with a 500 W high pressure Hg lamp through a 390 nm cutoff filter at 60 °C for 4 h. The consumption of **6a** (>99%) was monitored by ^{1}H NMR. The polymer products was collected by precipitation by adding to MeOH (12 mL) and subsequent suction filtration. The precipitation was repeated three times by concentration of the methanol solution, dissovling the remaind residues in DMF, and precipitated in methanol (DMF/methanol ~ 1/20). The combined precipitates were dried under reduced pressure at 50 °C to give a mixture of **2a**, **3a**, **4a** and **5a** (105 mg, 97%). The yields of **3a** and **5a** were determined as 9% and 15% from the ^{1}H NMR using methylene signals at ~4.2 ppm corresponding to the α-polymer end as an internal standard (Figure 2b, See also Figure S16 in Supporting Information). The SEC traces did not change before and after precipitation, and the *Disp*/(overall *Comb*) selectivity was determined to be 18/82 by the peak resolution method. (Figure 3a). The yied of **4a** (67%) was estimated by the total yield of the termination products, *Disp/(*overall *Comb*) selectivity, and the yield of **5a**.

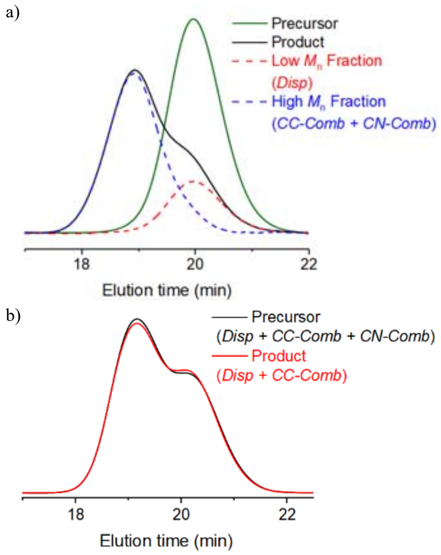


Figure 3. SEC traces of a) the termination reaction of **1a** starting from **6a** and b) before (black line) and after (red line) the thermal treatment of a mixture of **2a**, **3a**, **4a**, **5a** with the ratio of 20/20/42/18 in DMF at 100 ºC.

Typical experimental procedure for the thermal decomposition of 5b. A solution of **5b** (8.9 mg, 0.030 mmol) in C_6D_6 (0.60 mL) was heated at 120 °C in a NMR tube equipped with a greaseless PTFE piston, and the disappearance of **5b** and the formation of **2b**, **3b**, and **4b** were monitored by ^{1}H NMR. After complete consumption of **5b**, the yields of **2b**, **3b** and **4b** were determined as 5%, 1% and 82%, respectively. The *Disp/CC-Comb* selectivity determined by the yield of **2b** and **4b** was 11/89.

Typical experimental procedure for the thermal decomposition of 5a. A solution of a mixture **2a**, **3a**, **4a**, **5a** with the ratio of 20/20/42/18 formed by the termination study starting from **1b** (Table S1, run 27, 120 mg) in DMF (1.0 mL) was heated at 100 °C in a NMR Tube equipped with a greaseless PTFE piston. After complete disappearance of **5a** as monitored by ^{1}H NMR, the *Disp/CC-Comb* ratio was determined to be 43/57 by the peak resolution method of the SEC trace assuming the selective transformation from **5a** to **2a**, **3a**, and **4a** (Figure 3b). *Disp/CC-Comb* selectivity in the decomposition of **5a** was determined as 16/84 considering the amount of **5a** in the starting polymer.

Determination of diffusion constants. Diffusion constant (D) was determined by the diffusion ordered spectroscopy (DOSY) NMR experiments. Propionitrile or end-hydrogenated PAN **2a** was used as a model compound of **1b** or **1a**, respectively. **2a** was prepared by the reduction of **6a** by PhSH as reported.[34] DOSY NMR was performed using *ledbpgp2s* pulse sequence for the solutions of propionitrile or **2a** (M_n = 2400, $Đ$ = 1.10) (0.050 mol L^{-1}) in a NMR tube. The measurements using EC, PEG400, hexane, CH_2Cl_2, and THF solution were carried out without signal lock using *ledbpgppr2s* pulse sequence with presaturation of the solvent signals. The measurements were used the diffusion time Δ (D20) of 0.06 sec, and the appropriate diffusion gradient length δ (twice of P30) was determined experimentally in each measurement, with which the ratio between the maximum and minimum signal intensities in the examined gradient strength range (5%-95%) was within 0.05-0.1.

RESULTS AND DISCUSSION

1. Confirmation of the generation of radical 1 from 6. Quantitative formation of radical **1b** from **6b** by the photolysis was unambiguously confirmed by the ESR spectroscopy and a trapping experiment by TEMPO. The ESR of **1b** at 25 °C in C_6H_6 resonated at g = 2.00258 as doublet of quartet of triplets with the hyperfine coupling constants of 2.281, 2.027, and 0.341 mT with hydrogens at α and β to the nitrile group and nitrogen atom, respectively (Figure 1a). The spectrum was identical to the data obtained by the oxidation of propionitrile within the experimental error.[32] Furthermore, the photolysis of **6b** in the presence of TEMPO (1.1 equiv.) quantitatively gave the corresponding TEMPO-adduct. Generation of PAN-end radical **1a** from **6a** by photolysis was also confirmed by the ESR, which resonated at g = 2.00289 as doublet of triplet of triplet with the hyperfine coupling constants of 2.121, 2.071, and 0.379 mT with hydrogens at α and β to the nitrile group and nitrogen atom, respectively (Figure 1b).

2. Termination reaction of radical 1. At first, the termination of small model radical **1b** (R = H) was studied by photolyzing **6b** with a 500 W Hg lamp through a cut-off filter in C_6D_6 at 60 °C (Scheme 1). **6b** was completely consumed after 2 h, and **2b**, **3b**, **4b**, **5b**, and diphenylditelluride were formed with yields of 3, 4, 45, 44, and 100%, respectively, according to the ^{1}H NMR analysis. As part of **3b** (AN) might polymerize under the current conditions, the contribution of *Disp* was estimated from the quantity of **2b**. The *Disp*/*CC-Comb*/*CN-Comb* ratio was calculated as 8/47/45 (Table 1, run 1). *CN-Comb* product **5b** was isolated by a separate experiment and characterized by NMR and mass spectrometry. In the ^{1}H NMR, **5b** showed characteristic signals at 4.80 and 4.24 ppm, corresponding to the hydrogen α to the imine nitrogen (H^a) and the alkene (H^b) (Figure 2a) in DMSO-d_6. **5b** is stable at 60 °C for the time scale of this experiment but decomposition at high temperature (see below for details). The overall *Comb* selectivity (*CN-Comb* + *CC-Comb*) is 92%, which is consistent with previous results.[12-15]

The effect of the reaction conditions was next examined by changing the solvent and temperature. The same experiments in C_6D_6 at 50, 40 and 25 °C showed similar selectivity, but a slight increase in *Disp* and a decrease in *CC-Comb* were observed by lowering the temperature (runs 2-4). In contrast, the *CN-Comb* selectivity was insensitive to temperature. As a result, the overall *Comb* selectivity slightly dropped to 87% at 25 °C. When dimethyl formamide (DMF), ethylene carbonate (EC) or polyethylene glycol 400 (PEG400) was used as a solvent, the *Disp/CC-Comb/CN-Comb* selectivity significantly changed (runs 5-15). For example, the *Disp/CC-Comb/CN-Comb* selectivity in DMF, EC, and PEG400 at 60 °C was 18/70/12, 28/59/13 and 79/20/1, respectively. Despite these significant differences, the effect of temperature in the same solvent was marginal and showed the same trend as that observed in C_6D_6. There was a slight increase and decrease in the selectivity of *Disp* and *CC-Comb*, respectively, with an increase in viscosity, while *CN-Comb* was insensitive to this change.

The plots of the *Disp/CC-Comb* selectivity against the inverse of temperature in Kelvin and the bulk viscosity (η_{bulk}), which were independently determined by a viscometer, show an excellent linear correlation in the same solvent (Figures 4a and 4b). The results are consistent with the previous results.[19, 35, 36] in which increase of the viscosity by changing solvent and lowering temperature leads to the increase of the *Disp*. The general correlation regardless of the solvent used was obtained when the *Disp/CC-Comb* selectivity was plotted against the inverse of the diffusion coefficient, as determined by the diffusion constant from ^{1}H NMR DOSY experiments using propionitrile as a model for radical **1b** (Figure 4c, see the Table S2 for details). As the diffusion constant is inversely proportional to the microviscosity in the Stokes-Einstein equation, the results clearly indicate the importance of microviscosity as a general parameter for determining the *Disp/CC-Comb* selectivity, and the results are consistent with our recent report on the termination mechanism in styrene and methacrylate polymerization.[19] However, the *CN-Comb* selectivity is totally insensitive to the temperature and viscosity.

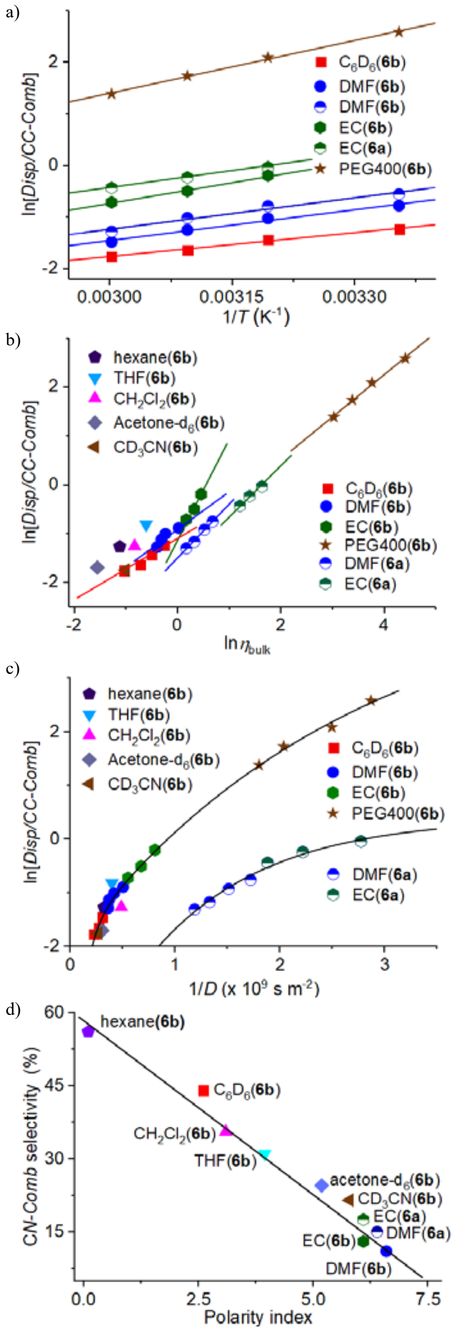


Figure 4. Parameters controlling the termination selectivity in the termination reaction starting with **6b** and **6a**. The correlation between the *Disp*/*CC-Comb* selectivity and a) the inverse of temperature in Kelvin, b) the bulk viscosity, and c) the microviscosity, and d) the *CN-Comb* selectivity and solvent polarity. Polarity index of propylene carbonate was used for that of ethylene carbonate.

To clarify the possible controlling element(s) of the *CN-Comb* pathway, the effect of polarity was examined because the formation of a polar C-N bond would be affected by the polarity of the medium. Although we anticipated an increase in the *CN-Comb* pathway in a polar solvent, it decreased as the solvent polarity increased, as studied in hexane, CH_2Cl_2, tetrahydrofuran (THF), acetone-d_6, CD_3CN (runs 16-20). In highly polar solvents, such as PEG400, virtually no *CN-Comb* termination occurred.

There is an excellent linear correlation between *CN-Comb* and the solvent polarity parameter reported by Snyder (Figure 4d).[37-39] While the detailed mechanism of the polar effect is unclear, the results can be explained that the transition state undergoing *CN-Comb* is hindered in a polar solvent rather than accelerated in a nonpolar solvent because the termination reaction is a diffusion-controlled reaction so that further rate enhancement is less likely. One possibility of this effect would be the stabilization of radical **1** by a polar medium.

When the results were plotted against other polarity parameters, such as that reported by Reichardt,[40] a good correlation was also observed (see the SI for details). However, Snyder's parameter fits better than the others. Snyder's parameter is obtained from the partition coefficient, while Reichardt's parameter is derived from the changes in the absorption spectra, i.e., solvatochromism. Therefore, the difference implies the origin of the observed polarity effect and further studies are necessary to clarify this point.

It is also worth noting that the *Disp/CC-Comb* selectivity obtained in these five solvents can be predicted by the microviscosity (runs 16-20 and Figure 4c), indicating that the *Disp/CC-Comb* selectivity is determined after the *CN-Comb* pathway is determined. We believe that all these results can be explained only by the presence of two termination-controlled domains, i.e., the polarity- and viscosity-controlled domains. The polarity-controlled domain comes first, which determines the contribution of the *CN-Comb* pathway, followed by the viscosity-controlled domain determining the *Disp* vs. *CC-Comb* pathways.

The *Disp/*(overall *Comb*) selectivity was almost completely inverted from 8/92 to 92/8 by changing the solvent from non-polar and non-viscous C_6D_6 to highly polar and viscous PEG400 (run 1 vs. run 15). The results suggest the potential for external control of the termination reaction.

Next, the termination mechanism of PAN radical **1a** was studied starting with **6a** (R = PAN, M_n = 2400, $Đ$ = 1.10, Fidelity = 95%) under the same conditions used for **6b** (runs 21-27). The generation of **1a** was also confirmed by the ESR using an oligomeric PAN sample. Due to the limited solubility of **6a**, only DMF and EC were used as solvents. The formation of *CN-Comb* product **5a** was suggested by the characteristic absorption at 4.44 and 5.03 ppm corresponding to the alkenic H^B and allylic H^A hydrogens in the ^{1}H NMR, respectively (Figure 2b). The quantity of **5a** was determined by comparing the characteristic absorption at 4.09 ppm corresponding to the ethoxy methylene signal originating from the α-polymer end of **6a**. This is also the first example of the experimental detection of *CN-Comb* product **5a**.

The *Disp/*(overall *Comb*) selectivity was determined by the peak resolution method of size exclusion chromatography (Figure 3a), and the quantity of *CC-Comb* product **4a** was calculated by subtracting the quantity of the *CN-Comb* product determined by ^{1}H NMR from the quantity of the overall *Comb* product. The quantity of *Disp* product **2a** determined by ^{1}H NMR from the characteristic alkene signals at 6.12 and 6.69 ppm (Figure 2b) agreed well with that determined by SEC. The *Disp/CC-Comb/CN-Comb* selectivity in DMF and EC at 60 °C was determined to be 18/67/15 and 32/50/18, respectively (runs 21 and 25).

The temperature and viscosity effects on the selectivity of **1a** showed the same trend as those observed with **1b** (runs 21-27). The selectivity of *Disp* increased and that of *CC-Comb* decreased as the temperature decreased and the viscosity increased, while the *CN-Comb* selectivity was insensitive to these changes. In addition, although the *Disp/CC-Comb* selectivity has an excellent correlation with the inverse of temperature and the bulk viscosity in each solvent (Figure 4a and 4b), the microviscosity is a general parameter for determining selectivity regardless of the solvent (Figure 4c). The different dependency of the *Disp/CC-Comb* selectivity on the microviscosity for radicals **1a** and **1b** should be due to the differences in molecular weights because the volume of a molecule also determines the diffusion constant and microviscosity.

The *CN-Comb* of **1a** also showed the same trend with that of **1b** in the same solvent, which is consistent with the presence of a polarity-controlled domain prior to the viscosity-controlled domain in the termination reaction. The slight drop of the *CN-Comb* selectivity of **1a** than **1b** would be attributed to the decrease of polarity due to the presence of PAN chain as indicated by the low polarity index of CH_3CN than DMF and EC.

3. Proposed mechanism for the polarity and viscosity effect. The termination mechanism of the diffused PAN-end radical $\mathbf{1}_{\mathbf{(dif)}}$ can be explained by considering two reaction domains, i.e., the polarity-controlled and viscosity-controlled domains, in the collision model (Figure 5).[19, 26, 27, 36] An encountered singlet radical pair undergoing the termination reaction, which forms two $\mathbf{1}_{\mathbf{(dif)}}$ radicals with orthogonal conformations, because a triplet radical pair has to be transformed to a singlet pair by intersystem crossing. Then, the singlet radical pair first experiences the polarity-controlled domain, in which the contribution of *CN-Comb* is determined and gives **5**. The viscosity is probably unimportant in the formation of **5** because a negligible conformational change is required from the singlet radical pair to the corresponding transition state. The stabilization of polar radical **1** by the polar solvent would decelerate this pathway. Then, the viscosity-controlled domain starts, in which *Disp* increases as the viscosity increases for the same reasons as in the case of the termination of methacrylates and styrene;[19] the conformational change undergoing *CC-Comb* is larger than that undergoing *Disp*, and the former pathway is more sensitive to the viscosity than the latter pathway.

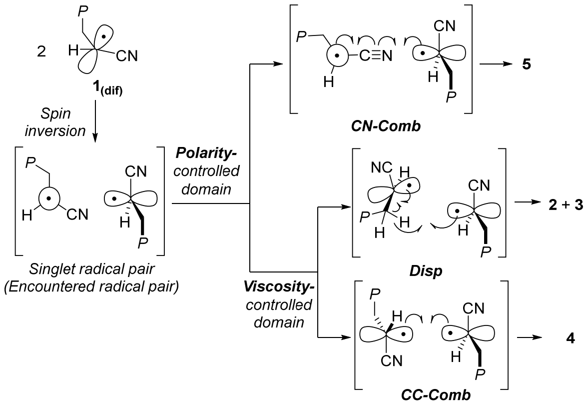


Figure 5. Advanced collision model for the termination of a PAN chain-end radical; P refers to the PAN chain.

4. Thermal stability and termination mechanism of *CN-Comb* adduct 5.

The *CN-Comb* product **5b** decomposed at high temperatures following first-order kinetics and gave *Disp* and *CC-Comb* products **2b**, **3b**, and **4b** (Scheme 1). The *Disp/CC-Comb* selectivity in C_6D_6 and in DMF had marginal temperature dependency, and the *Disp* selectivity decreased as the temperature increased in the experiments carried out at 60-120 °C (Table 2, runs 1-7). The *CC-Comb* product **4b** was mainly obtained in all cases with 84-89% selectivity. In contrast, the decomposition of **5b** in PEG400 produced a considerable quantity of *Disp* products, and the *Disp/CC-Comb* selectivity decreased from 60/40 at 60 °C to 50/50 at 100 °C (runs 8-10). The results are in marked contrast to the *Disp/CC-Comb* selectivity shown in Table 1, but this is reasonable because the decomposition of **5b** initially generates the caged radical pair (**1b**$_{\mathbf{(cage)}}$), and the *Disp/CC-Comb* selectivity in the termination of the caged radical is much less sensitive than the diffused radical.[26,41]

When the *CN-Comb* took place, the decomposition kinetics of **5b** should be affected. However, quantification of its contribution cannot be carried out because of the difficulty in determining the *CN-Comb* termination inside a solvent cage. However, all decomposition reaction nicely followed the first order kinetics despite the amount of regenerated **5b** was unclear. This is probably because the selectivity of the *CN-Comb* pathway is essentially constant under the current conditions.

The decomposition of **5b** in DMF and PEG400 at 60-100 °C took place 2-9 times faster than that in C_6D_6. For example, the apparent first-order rate constants at 80 °C in C_6D_6, DMF, and PEG400 are 3.1×10^{-6}, 1.7×10^{-5}, and 6.4 × 10-6 s^{-1}, respectively (see the Table S4 in the SI for details). When the same *CN-Comb* selectivity inside and outside a solvent cage is assumed, the decomposition in DMF takes place much faster than that in C_6D_6. The apparent activation energy of the C-N bond cleavage of **5b** in C_6D_6, DMF, and PEG400 was determined to be 113, 97, and 102 kJ mol^{-1}, respectively. These values are very similar to the C-N bond dissociation energy of **5b** (125 kJ mol^{-1}) calculated by density functional theory at the B3LYP/6-31G/6-31+G(d,p) level of theory. The observed polar effect in the C-N bond dissociation is reasonable considering the polar characteristics of the C-N bond. However, it is unclear whether the observed polar effect is related to the insensitivity of *CN-Comb* formation in the termination reaction. Further studies are needed to clarify this point.

The decomposition of *CN-Comb* product **5a** in DMF was examined by heating a mixture of **2a**, **3a**, **4a**, and **5a** (*Disp/CC-Comb*/*CN-Comb* = 40/42/18), and the disappearance of the characteristic

H^A and H^B signals at 5.03 and 4.44 ppm of **5a** was monitored at 60-100 °C (runs 12-14). After complete consumption of **5a**, the *Disp/CC-Comb* selectivity was determined by the SEC peak resolution method assuming the selective transformation from **5a** to **2a**, **3a**, and **4a**. The *CC-Comb* pathway was dominant, and the effect of the *Disp/CC-Comb* selectivity was more apparent in **5a** than in **5b**, with values of 20/80 at 60 °C and 16/84 at 100 °C. This result may be due to the molecular weight because it significantly affects the viscosity. The decomposition rate of **5a** was approximately 2 times slower than that of **5b**, and these results must also be due to the molecular weight effect.

Radical polymerization of AN is usually carried out under mild thermal conditions, such as 60 °C, suggesting the presence of a certain quantity of *CN-Comb* product **5a**. When such a fresh sample is treated for processing, such as the molding process, **5a** is transformed into **2a**, **3a**, and **4a** at high temperatures. This process was modeled by heating **5b** and **5a** in bulk at 100 °C (runs 11 and 15). While the contribution of *Disp* was 55% when starting with **5b**, complete *Disp* selectivity (>99%) was observed when starting with **5a**. The difference is most likely due to the difference in viscosity. The results suggest that care must be taken in the processing step because the physical properties could be altered due to changes in the *Disp* and *CC-Comb* compositions.

CONCLUSIONS

For the first time, the termination mechanism in the radical polymerization of AN was clarified, and the contribution of *CN-Comb* was experimentally proven. Although the termination reaction is classified as an ultrafast reaction, the termination is divided into two fate changing domains: the polarity-controlled domain affecting the *CN-Comb* pathway and the viscosity-controlled domain affecting the *Disp* and *CC-Comb* pathways. *CN-Comb* product **5** decomposes at high temperatures and gives *Disp* and *CC-Comb* products. As **5** generates a solvent-caged radical pair of $\mathbf{1}_{\mathbf{(cage)}}$, the termination mechanism starting with **5** is different from that of free, diffused PAN-end radical $\mathbf{1}_{\mathbf{(dif)}}$. Therefore, care must be taken due to the possible changes in the compositions and physical properties of PAN samples during processing, such as the molding process. Furthermore, while the coupling reaction of two radical species has recently been recognized as an important synthetic reaction in polymer and organic synthesis,[23-25, 42-45] the scope of the reaction are still limited. This work would also shed a new light for designing highly efficient coupling reaction.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge via the Internet at http://pubs.acs.org.

Synthetic procedures, procedures of photochemical reactions and the analysis, NMR DOSY experiments, and computational methods.

AUTHOR INFORMATION

Corresponding Author

Shigeru Yamago - Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan; orcid.org/0000-0002-4112-7249; Email: yamago@scl.kyoto-u.ac.jp

Yasuyuki Nakamura - Data-Driven Polymer Design Group, Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan; orcid.org/0000-0003-0078-6413; Email: NAKAMURA.Yasuyuki@nims.go.jp

Funding Sources

This work was supported by the Japan Society for the Promotion of Science KAKENHI (Grant Nos. 19K05593 (Y.N.) and 16H06352 (S.Y.)) and the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (Grant No. 2020-20)Notes

The authors declare no competing financial interests.

ABBREVIATIONS

AN, acryronitrile, *CC-Comb*, combination by carbon-carbon bond formation, *CN-Comb*, combination by carbon-nitrogen bond formation, *Disp*, disproportionation, ESR, electron spin resonance spectroscopy, NMR, nuclear magnetic resonance spectroscopy, SEC, size exclusion chromatography.

Table 1. Termination mechanism of diffused PAN chain-end radical **1** generated from **6**

run	precursor	solvent	temp.	η_bulk	*D*	polarity	selectivity (%)		
	(**6**)		(°C)	(mPa·s)[b]	(x 10^{-9} $m^2 \cdot s^{-1}$)[c]	Index[d]	*Disp*	*CC-Comb*	*CN-Comb*
1	**6b**	C_6D_6	60	0.36	4.3	2.1	8	47	45
2	**6b**	C_6D_6	50	0.49	3.7	2.1	9	45	46
3	**6b**	C_6D_6	40	0.61	3.3	2.1	11	43	46
4	**6b**	C_6D_6	25	0.78	2.8	2.1	13	41	46
5	**6b**	DMF	60	0.60	2.8	6.4	18	70	12
6	**6b**	DMF	50	0.74	2.6	6.4	22	67	11
7	**6b**	DMF	40	0.80	2.4	6.4	25	63	12
8	**6b**	DMF	25	1.04	2.1	6.4	28	61	11
9	**6b**	EC[e]	60	1.2	1.8	6.1[f]	28	59	13
10	**6b**	EC[e]	50	1.4	1.5	6.1[f]	33	55	12
11	**6b**	EC[e]	40	1.6	1.3	6.1[f]	39	49	12
12	**6b**	PEG400	60	21	0.68	-[g]	79	20	<1
13	**6b**	PEG400	50	30	0.49	-[g]	84	15	<1
14	**6b**	PEG400	40	44	0.40	-[g]	88	11	<1
15	**6b**	PEG400	25	84	0.36	-[g]	92	7	<1
16	**6b**	Hexane	25	0.33	3.1	0.1	10	36	54
17	**6b**	CH_2Cl_2	25	0.44	2.5	3.1	14	50	36
18	**6b**	THF	25	0.55	2.0	4.0	21	48	31
19	**6b**	Acetone-d_6	25	0.35	3.2	5.1	11	61	28
20	**6b**	CD_3CN	25	0.37	3.7	5.8	11	64	25
21	**6a**	DMF	60	1.2	0.84	6.4	18	67	15
22	**6a**	DMF	50	1.4	0.75	6.4	20	65	15
23	**6a**	DMF	40	1.7	0.69	6.4	23	62	15
24	**6a**	DMF	25	2.0	0.60	6.4	27	58	15
25	**6a**	EC[d]	60	3.4	0.56	6.1[f]	32	50	18
26	**6a**	EC[d]	50	4.1	0.45	6.1[f]	36	46	18
27	**6a**	EC[d]	40	5.2	0.36	6.1[f]	40	42	18

a) A solution of **6b** (0.050 mol L^{-1}) or **6a** (M_n = 2400, *Đ* = 1.10, 0.12 mg mL^{-1}) was irradiated with a 500 W high-pressure Hg lamp through a 390 nm cut-off filter for 2-10 h. b) The bulk viscosity of the reaction solution was determined by a viscometer. c) Diffusion constant of **6** in the reaction solution, as determined by ^1H DOSY NMR experiments using **3a** and **3b** as the models of radicals **1a** and **1b**, respectively. See the Supporting information for details. d) Data taken from ref.[37, 38]. e) Ethylene carbonate. f) Data of propylene carbonate was used. g) Data were unavailable.

Table 2. Termination mechanism of PAN chain-end radical **1** starting from **5**[a]

run[a]	precursor	solvent	temp. (°C)	selectivity (%)[b] *Disp*	selectivity (%)[b] *CC-Comb*
1	**5b**	C_6D_6	60	14	86
2	**5b**	C_6D_6	80	13	87
3	**5b**	C_6D_6	100	12	88
4	**5b**	C_6D_6	120	11	89
5	**5b**	DMF	60	16	84
6	**5b**	DMF	80	14	86
7	**5b**	DMF	100	12	88
8	**5b**	PEG400	60	60	40
9	**5b**	PEG400	80	55	45
10	**5b**	PEG400	100	50	50
11	**5b**	bulk	100	55	45
12	**5a**	DMF	60	20	80
13	**5a**	DMF	80	18	82
14	**5a**	DMF	100	16	84
15	**5a**	bulk	100	>99	<1

a) A solution of **5b** (0.050 mol L^{-1}) or a mixture of **5a, 2a**, **3a**, and **4a** (0.12 mg L^{-1}) prepared from **1a** was heated for 2-10 h for runs 1-11 and 12-15, respectively. b) Determined by ^{1}H NMR for runs 1-11 and SEC analysis for runs 12-15. See the main text for details.

REFERENCES

1. Odian, G., *Principles of Polymerization 4th Edition*. Wiley-Interscience: Canada, **2004**.
2. Moad, G.; Solomon, D. H., *The Chemistry of Radical Polymerization 2nd Edition*. Elsevier: Amsterdam, **2006**.
3. Krevelen, D. W. V.; Nijenhuis, K. T., *Properties of Polymers Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions 4th Edition. Elsevier Science*: Slovenia, **2009**.
4. Yamago, S.; Kayahara, E.; Yamada, H., Synthesis of Structurally Well-Controlled ω-Vinylidene Functionalized Poly(alkyl methacrylate)s and Polymethacrylonitrile by Organotellurium, Organostibine, and Organobismuthine-Mediated Living Radical Polymerizations. *React. Funct. Polym.* **2009**, *69*, 416-423.
5. Elias, H.-G., *Macromolecules*. Viley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2007**; Vol. 2.
6. Elias, H.-G., *Macromolecules*. Viley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2009**; Vol. 4.
7. Chae, H. G.; Choi, Y. H.; Minus, M. L.; Kumar, S., Carbon Nanotube Reinforced Small Diameter Polyacrylonitrile Based Carbon Fiber. *Compos. Sci. Technol.* **2009**, *69*, 406-413.
8. Munir, M. M.; Nuryantini, A. Y.; Khairurrijal, K.; Abdullah, M.; Iskandar, F.; Okuyama, K., Preparation of Polyacrylonitrile Nanofibers with Controlled Morphology Using a Constant-Current Electrospinning System for Filter Applications. *Mater. Sci. Forum* **2013**, *737*, 159-165.
9. Vinh, N. D.; Kim, H.-M., Electrospinning Fabrication and Performance Evaluation of Polyacrylonitrile Nanofiber for Air Filter Applications. *Appl. Sci.* **2016**, *6*, 235-245.

10. Otvagina, K. V.; Penkova, A. V.; Dmitrenko, M. E.; Kuzminova, A. I.; Sazanova, T. S.; Vorotyntsev, A. V.; Vorotyntsev, I. V., Novel Composite Membranes Based on Chitosan Copolymers with Polyacrylonitrile and Polystyrene: Physicochemical Properties and Application for Pervaporation Dehydration of Tetrahydrofuran. *Membranes* **2019**, *9*, 38-57.
11. Serkov, A. T.; Radishevskii, M. B., Status and Prospects for Production of Carbon Fibres Based on Polyacrylonitrile. *Fibre Chem.* **2008**, *40*, 24-31.
12. Bamford, C. H.; Jenkins, A. D.; Johnston, R., The Termination Reaction in the Polymerization of Acrylonitrile. *Trans. Faraday Soc.* **1959**, *55*, 179-184.
13. Bevington, J. C.; Eaves, D. E., Initiation the Polymerization of Acrylonitrile. *Trans. Faraday Soc.* **1959**, *55*, 1777-1782.
14. Bailey, B. E.; Jenkins, A. D., The Mechanism of Termination in the Polymerization of Acrylonitrile. *Trans. Faraday Soc*. **1960**, *56*, 903-906.
15. Bamford, C. H.; Dyson, R. W.; Eastmond, G. C., Network Formation IV. The Nature of the Termination Reaction in Free-Radical Polymerization. *Polymer* **1969**, *10,* 885-899.
16. Nakamura, Y.; Yamago, S., Termination Mechanism in the Radical Polymerization of Methyl Methacrylate and Styrene Determined by the Reaction of Structurally Well-Defined Polymer End Radicals. *Macromolecules* **2015**, *48*, 6450-6456.
17. Nakamura, Y.; Lee, R.; Coote, M. L.; Yamago, S., Termination Mechanism of the Radical Polymerization of Acrylates. *Macromol. Rapid Commun*. **2016**, *37*, 506-513.
18. Nakamura, Y.; Ogihara, T.; Yamago, S., Mechanism of Cu(I)/Cu(0)-Mediated Reductive Coupling Reactions of Bromine-Terminated Polyacrylates, Polymethacrylates, and Polystyrene. *ACS Macro Lett.* **2016**, *5*, 248-252.

19. Nakamura, Y.; Ogihara, T.; Hatano, S.; Abe, M.; Yamago, S., Control of the Termination Mechanism in Radical Polymerization by Viscosity: Selective Disproportionation in Viscous Media. *Chem. Eur. J.* **2017**, *23*, 1299-1305.

20. Yamago, S., Precision Polymer Synthesis by Degenerative Transfer Controlled/Living Radical Polymerization Using Organotellurium, Organostibine, and Organobismuthine Chain-Transfer Agents. *Chem. Rev.* **2009**, *109*, 5051-5068.

21. Yamago, S.; Iida, K.; Yoshida, J., Organotellurium Compounds as Novel Initiators for Controlled/Living Radical Polymerizations. Synthesis of Functionalized Polystyrenes and End-Group Modifications. *J. Am. Chem. Soc.* **2002**, *124*, 2874-2875.

22. Goto, A.; Kwak, Y.; Fukuda, T.; Yamago, S.; Iida, K.; Nakajima, M.; Yoshida, J., Mechanism-Based Invention of High-Speed Living Radical Polymerization Using Organotellurium Compounds and Azo-Initiators. *J. Am. Chem. Soc.* **2003**, *125*, 8720-8721.

23. Yamago, S., Photoactivation of Organotellurium Compounds in Precision Polymer Synthesis: Controlled Radical Polymerization and Radical Coupling Reactions. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 287-298.

24. Nakamura, Y.; Arima, T.; Tomita, S.; Yamago, S., Photoinduced Switching from Living Radical Polymerization to a Radical Coupling Reaction Mediated by Organotellurium Compounds. *J. Am. Chem. Soc.* **2012**, *134*, 5536-5539.

25. Nakamura, Y.; Arima, T.; Yamago, S., Modular Synthesis of Mid-Chain-Functionalized Polymers by Photoinduced Diene- and Styrene-Assisted Radical Coupling Reaction of Polymer-End Radicals. *Macromolecules* **2014**, *47*, 582-588.

26. Li, X.; Ogihara, T.; Abe, M.; Nakamura, Y.; Yamago, S., The Effect of Viscosity on the Diffusion and Termination Reaction of Organic Radical Pairs. *Chem. Eur. J.* **2019**, *25*, 9846-9850.

27. Li, X.; Kato, T.; Nakamura, Y.; Yamago, S., The Effect of Viscosity on the Coupling and Hydrogen-Abstraction Reaction between Transient and Persistent Radicals. *Bull. Chem. Soc. Jpn.* **2021**, accepted (doi:10.1246/bcsj.20200398).

28. Barry, J. T.; Berg, D. J.; Tyler, D. R., Radical Cage Effects: Comparison of Solvent Bulk Viscosity and Microviscosity in Predicting the Recombination Efficiencies of Radical Cage Pairs. *J. Am. Chem. Soc.* **2016**, *138*, 9389-9392.

29. Barry, J. T.; Berg, D. J.; Tyler, D. R., Radical Cage Effects: The Prediction of Radical Cage Pair Recombination Efficiencies Using Microviscosity Across a Range of Solvent Types. *J. Am. Chem. Soc.* **2017**, *139*, 14399-14405.

30. Boyd, D. B., β-Methylene-D, L-asparagine. *J. Org. Chem.* **1985**, *50*, 882-885.

31. Kayahara, E.; Yamago, S.; Kwak, Y.; Goto, A.; Fukuda, T., Optimization of Organotellurium Transfer Agents for Highly Controlled Living Radical Polymerization *Macromolecules* **2008**, *41*, 527-529.

32. Livingston, R.; Zeldes, H., Paramagnetic Resonance Study of Liquids During Photolysis VII. Nitrilest. *J. Mag. Res.* **1969**, *1*, 169-177.

33. Hammill, C. L.; Noble, B. B.; Norcott, P. L.; Ciampi, S.; Coote, M. L., Effect of Chemical Structure on the Electrochemical Cleavage of Alkoxyamines. *J. Phys. Chem. C* **2019**, *123*, 5273-5281.

34. Yamago, S.; Matsumoto, A., Arylthiols as Highly Chemoselective and Environmentally Benign Radical Reducing Agents. *J. Org. Chem.* **2008**, *73*, 7300-7304.

35. Fischer, H.; Paul, H., Rate Constants for Some Prototype Radical Reactions in Liquids by Kinetic Electron Spin Resonance. *Acc. Chem. Res.* **1987**, *20*, 200-206.

36. Schuh, H.-H.; Fischer, H., The Kinetics of the Bimolecular Self-Reaction of t-Butyl Radicals in Solution. II. Disproportionation/Combination Ratios. *Helv. Chim. Acta* **1978**, *61*, 2463-2481.

37. Barwick, V. J., Strategies for Solvent Selection - a Literature Review. *Trends Anal. Chem.* **1997**, *16*, 293-309.

38. Snyder, L. R., Classification off the Solvent Properties of Common Liquids. *J. Chromatogr. Sci.* **1978**, *16*, 223-234.

39. Because the polarity parameter of EC was unavailable, that of propylene carbonate was used.

40. Reichardt, C., Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* **1994**, *94*, 2319-2358.

41. Tanner, D. D.; Rahimi, P. M., Disproportionation-Combination Reactions of Caged Geminate Radical Pairs Formed from the Photo Decomposition of 2,2'-Azoisobutane. Anisotropic Reorientation of tert-Butyl Radicals in Viscous Media and Birth Effects in very Viscous Media. *J. Am. Chem. Soc.* **1982**, *104*, 225-229.

42. Debuigne, A.; Jérôme, C.; Detrembleur, C., Isoprene Assisted Radical Coupling of (Co)polymers Prepared by Cobalt-Mediated Radical Polymerization. *Angew. Chem. Int. Ed.* **2009**, *121*, 1450-1452.

43. Debuigne, A.; Poli, R.; De Winter, J.; Laurent, P.; Gerbaux, P.; Wathelet, J.-P.; JéRôMe, C.; Detrembleur, C., Effective Cobalt-Mediated Radical Coupling (CMRC) of Poly(vinyl acetate) and Poly(N-vinylpyrrolidone) (Co)polymer Precursors. *Macromolecules* **2010**, *43*, 2801-2813.

44. Masuda, K.; Nagatomo, M.; Inoue, M., Direct Assembly of Multiply Oxygenated Carbon Chains by Decarbonylative Radical-Radical Coupling Reactions. *Nat. Chem.* **2017**, *9*, 207-212.

45. Kawamata, T.; Yamaguchi, A.; Nagatomo, M.; Inoue, M., Convergent Total Synthesis of Asimicin via Decarbonylative Radical Dimerization. *Chem. Eur. J.* **2018**, *24*, 18907-18912.

Table of Content