Polymerization of 1,3-Dienes with Functional Groups. 4. Anionic Polymerization of \(N,N\)-diethyl-2-methylene-3-butenamide

Katsuhiko Takenaka*, Natsuyo Shibata, Shinsuke Tsuchida, Hiroki Takeshita, Masamitsu Miya, and Tomoo Shiomi

Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940–2188, Japan
* Corresponding author: ktakenak@vos.nagaokaut.ac.jp

Received February 21, 2008; Accepted May 2, 2008
© 2008 The Society of Rubber Industry, Japan

Abstract Anionic polymerization of \(N,N\)-diethyl-2-methylene-3-butenamide (DEA), which is a 1,3-butadiene derivative containing a diethylamide function, was carried out in tetrahydrofuran (THF) under various conditions. When DEA was polymerized in THF at \(-78^\circ\)C using potassium naphthalenide (K-Naph) or diphenylmethylpotassium (DPMK) as an initiator, a polymer of predictable molecular weight with a narrow molecular weight distribution was obtained. However, the rate of polymerization was extremely slow to reach 80% conversion after 720 h. When the polymerization temperature was raised to 20°C, a low molecular weight oligomer with a broad molecular weight distribution was obtained because of a chain transfer reaction. On the other hand, no such side reaction occurred even at 20°C, when polymerization was carried out in the presence of LiCl. Also, the chain transfer reaction did not occur in lithium naphthalenide (Li-Naph) initiated polymerization. The microstructure of the polymer prepared using a potassium counter cation was a 1:1 mixture of 1,4-\(E\) and 1,2- structures. In the case of Li-Naph or DPMK/LiCl systems, the microstructure was a complicated mixture of 1,4-\(E\), 1,4-\(Z\), and 1,2-structures.

Keywords \(N,N\)-Diethyl-2-methylene-3-butenamide, Anionic Polymerization, Microstructure, Chain-transfer Reaction, LiCl, Diphenylmethylpotassium.

Introduction

It is well known that anionic polymerization of non-polar 1,3-dienes such as isoprene is one of the best methods to prepare polydienes having a well-characterized chain structure\(^1\)-\(^4\). When the polymerization was carried out in a non-polar hydrocarbon solvent using butyllithium as an initiator, polydienes mainly having 1,4-structures were formed. In addition, the living nature of this polymerization system enables the formation of polymers having predictable molecular weight with narrow molecular weight distributions. In the case of 1,3-dienes with polar functional groups, the situation is very different. Such functional groups directly attached to the butadienyl skeleton occasionally make the monomer unstable. In fact, 2-ethoxyacrylonitrile-1,3-butadiene, an ethyl ester of 1,3-butadiene-2-carboxylic acid, can not exist at ambient temperature since this monomer has a strong tendency to dimerize by the Diels–Alder reaction\(^5\). Among the various types of carbonyl-substituted 1,3-butadienes, dialkylamide-substituted 1,3-butadienes are one of the exceptions because they can be isolated as monomers even at room temperature.

In our previous studies, we have reported the free-radical polymerization of \(N,N\)-dialkyl-2-methylene-3-butenamides\(^6\)-\(^7\). Although there have been several reports on the anionic polymerization of \(N,N\)-dialkylacrylamides\(^8\)-\(^10\), our reports were the first ones describing the polymerization behavior of their butadiene analogs. By studying their copolymerizations with styrene, it was found that these monomers had large \(Q\) and positive \(e\) values based on the Alflay and Price \(Q-e\) theory\(^11\). This indicates that the dialkylamide-substituted 1,3-butadiene derivatives can potentially be polymerized using anionic initiators. By selecting appropriate polymerization conditions, polymers of controlled molecular weight with narrow molecular weight distributions, having microstructures different from the one obtained by free-radical polymerization, could be obtained. In this study, we report the anionic polymerization behavior of \(N,N\)-diethyl-
2-methylene-3-butenamide (DEA) and the microstructure of the resulting polymers.

Experimental

Materials

The synthetic procedure of DEA has been described elsewhere. The monomer was stirred for 12 h with calcium hydride, and was distilled under high-vacuum conditions. It was then diluted using dry tetrahydrofuran (THF) and sealed in glass ampoules with break-seals. Lithium and potassium naphthalenides (Li-Naph, K-Naph) were prepared according to well-known procedures. Their actual concentrations were determined by measuring the molecular weight of polystyrene, which is prepared using an appropriate amount of alkaline metal naphthalenide initiator and an accurate amount of styrene by assuming that the polymerization was living in nature. Diphenylmethylpotassium (DPMK) was prepared by the reaction of K-Naph and a slightly excess amount of diphenylmethane. Anhydrous LiCl (Merck) was dried in vacuum at 100°C for 48 h and then dissolved in dry THF.

Anionic polymerization

All the polymerizations were carried out under high-vacuum conditions at desired temperatures. In a typical case, a monomer solution was added to the initiator solution at 78°C, and the temperature was maintained for 5 min. Then, the reactor was immersed in a controlled temperature bath at 78–20°C. In the case of polymerization using LiCl as an additive, the initiator and LiCl were mixed at room temperature for 5 min, and then were cooled to 78°C followed by the addition of monomer. The polymerization was quenched by the addition of a small amount of dilute hydrochloric acid, and the reaction mixtures were poured into water to precipitate the polymer. The polymer thus obtained was purified twice by reprecipitation from THF to n-hexane and finally freeze-dried from a benzene solution.

Measurements

$^1$H and $^{13}$C NMR spectra were recorded using a JEOL JNM-AL-400 spectrometer in CDCl$_3$. A solvent peak was used as a reference. Size exclusion chromatography (SEC) chromatogram was obtained at 40°C using a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH TSKgel HXL-4000, -3000, and -2000 (7.8 mm × 30 cm)) with UV and refractive index detectors. THF was used as a carrier solvent at a flow rate of 1 mL/min. Calibration curve was made to values with standard polystyrene samples. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-ToF MS) was performed using an Applied Biosystems Voyager DE-RP instrument. A small amount of sodium iodide was added to enhance the sample ionization, and 2,5-dihydroxybenzoic acid was used as the matrix.

Results and Discussion

Anionic polymerization of DEA

In the anionic polymerization of 1,3-dienes, the propagating chain end is a carbanion having strong nucleophilicity and basicity. Since the dialkylamide function is potentially susceptible to nucleophilic acyl substitution by a carbanion, the polymerization condition should be carefully selected to avoid such a side reaction. The polymerization mixture with potassium as a counter cation is shown in Figure 1. Upon addition of DEA to K-Naph at −78°C, the characteristic deep green color of the initiator immediately turned pale yellow in color. A similar tendency was observed when the monomer was added to DPMK at −78°C, although the original color of the initiator was deep orange. No further change of color was observed for up to 720 h, as long as the temperature was maintained below −78°C. On the other hand, when the temperature was raised to higher temperature such as 0 to 20°C after initiation, the polymerization mixture turned deep purple in color and retained this color until the end of polymerization. In addition, this change of color could not be reversed in spite of lowering the polymerization temperature again to −78°C. The color disappeared instantaneously by the addition of dilute hydrochloric acid but did not disappear by the addition of methanol. Although the origin of this color is currently unclear, it could be related with the chain-transfer reaction, which is discussed in a later section.

Table 1 summarizes the result of anionic polymerization. When the polymerization was carried out at −20–20°C with K-Naph and DPMK, low molecular weight oligomers
with broad molecular weight distributions were obtained regardless of the monomer-to-initiator ratios and polymerization time. In each case, a considerable amount of the monomer remained unreacted in the polymerization mixture. Since the oligomers thus formed were soluble in the common organic solvent including methanol, it was difficult to separate the oligomers from the residual monomer and other low molecular weight compounds to determine the conversion accurately. The SEC chromatogram of the oligomer shown in Figure 2(a) has a broad peak in the oligomer range. This could be a result of the chain-transfer reaction during the course of polymerization.

On the other hand, when polymerized at $-78^\circ$C, polymers of much higher molecular weight with narrow molecular weight distribution were obtained, although the conversion was not quantitative. In addition, it was necessary to polymerize for a long time ($\sim 720$ h) to achieve high conversion, indicating that the polymerization rate was extremely slow. However, the calculated molecular weight based on both the monomer-to-initiator ratio and the conversion agreed well with the value determined by SEC and MALDI-ToF MS. The SEC chromatogram of the polymer shown in Figure 2(b) was sharp and unimodal, indicating that the side reaction was suppressed by lowering the polymerization temperature.

As seen in Table 1, the molecular weight increases with increasing time and conversion with keeping its distribution narrow. This indicates that a stable active species was formed in the polymerization mixture.

When polymerization was carried out with Li-Naph, the polymerization behavior was different. The polymerization rate at $-78^\circ$C using lithium counter ions was also slow, although the molecular weight distribution was narrow. However, it should be noted that the polymerization rate

![Figure 1. Appearance of the polymerization mixture.](image)

![Figure 2. SEC chromatograms of polyDEA polymerized at (a) $-20^\circ$C and (b) $-78^\circ$C.](image)

Table 1. Anionic Polymerization of DEA under Various Conditions

| Initiator$^a$ | DEA (mmol) | [DEA]/[Initiator] | Temp. ($^\circ$C) | Time (h) | Conv.$^b$ (%) | $M_n \times 10^3$ | $M_w/M_n$ | $M_n$ \(\times 10^3\) | $M_w/M_n$ |
|--------------|------------|-------------------|-----------------|----------|---------------|-----------------|---------|----------------|---------|
| K-Naph       | 0.210      | 7.25              | 34.5            | 20       | 22            | nd              | 1.30    | 1.37           |         |
| DPMK         | 0.213      | 14.14             | 66.0            | 20       | 23            | nd              | 1.30    | 1.21           |         |
| DPMK         | 0.114      | 7.25              | 63.6            | 0        | 24            | nd              | 1.99    | 1.24           |         |
| DPMK         | 0.099      | 6.98              | 70.5            | $-20$    | 72            | nd              | 7.73    | 2.25           |         |
| DPMK         | 0.112      | 7.86              | 70.2            | $-50$    | 240           | 71              | 2.25    | 1.40           |         |
| DPMK         | 0.094      | 6.41              | 68.2            | $-78$    | 72            | 12              | 1.26    | 2.20           |         |
| DPMK         | 0.134      | 6.94              | 51.8            | $-78$    | 168           | 34              | 2.686   | 2.72           | 1.09    |
| DPMK         | 0.138      | 7.03              | 50.9            | $-78$    | 720           | 73              | 5.694   | 5.1            | 1.09    |
| Li-Naph      | 0.210      | 7.38              | 33.4            | $-78$    | 168           | 22              | 2.70    | 3.04           | 1.12    |
| Li-Naph      | 0.177      | 6.25              | 35.3            | 0        | 24            | 75              | 8.11    | 8.58           | 1.09    |
| DPMK/LiCl$^c$| 0.092      | 6.96              | 76.0            | 0        | 24            | 84              | 9.3     | 9.6            | 1.03    |
| DPMK/LiCl$^c$| 0.097      | 7.67              | 79.0            | 20       | 24            | 92              | 11.1    | 11.7           | 1.04    |

$^a$) DPMK: $\text{Ph}_2\text{CHK}$.

$^b$) nd: not determined.

$^c$) DPMK/LiCl was around 1/5.
was accelerated, and the polymer of controlled molecular weight with narrow distribution was obtained when polymerized at 0°C with Li-Naph. This indicates that the active chain end with a lithium counter ion is more stable compared with that with a potassium ion, and no chain-transfer occurred. The smaller ionic radii of lithium ions might have enabled the formation of tight ion pairs to stabilize the active chain end. It is interesting that the polymers with narrow molecular weight distributions were also obtained when a mixture of DPMK and LiCl was used as an initiator. LiCl is known to stabilize the active chain end carbanion of alkyl acrylates\textsuperscript{(12)} and alkyl methacrylates\textsuperscript{(13)} in their anionic polymerizations. It also affects the stereospecificity in the anionic polymerization of $N,N$-dialkylacrylamides\textsuperscript{(14)}. Considering the microstructure of the polymers obtained in this study, cation exchange from potassium to lithium occurred during the course of polymerization, and therefore, the chain-transfer was suppressed in this mixed initiator system.

Figure 3 shows the MALDI-ToF MS spectrum of the polymers prepared using potassium counter ions at different polymerization temperatures. It is obvious that the series of signals having 153 Da intervals corresponding to the polymer molecules having different degrees of polymerization was observed in each case. The multiple peaks in one group of signals can be attributed to the polymer fragments having different end groups and adduct ions. Figure 4 shows the $m/z$ axis expanded spectrum of the same samples. The signals at $m/z = 2322$ in Figure 4(a) corresponds to the Na$^+$ adduct of 15-mer of DEA having two hydrogen atoms at both chain ends, and the one at 2335 in Figure 4(b) is also an Na$^+$ adduct of 14-mer of DEA having one diphenylmethyl (DPM) moiety and a hydrogen atom at $\alpha$ and $\omega$ chain ends, respectively. In principle, polymers having a hydrogen terminated structure should be formed with K-Naph initiator whereas diphenylmethyl fragments should be present at the polymer chain-end with DPMK initiated polymerization, provided that no chain-transfer reaction occurs during the course of polymerization. Therefore, no polymer species having the same molecular weight should be obtained in the K-Naph initiated and the DPMK initiated polymers. On the contrary, it is obvious in Figure 4(b) that polymer fragments having the same molecular weight, $m/z = 2322$, were contained in the DPMK initiated polymer prepared at 20°C. This strongly indicates that this DPMK initiated polymer is contaminated with polymers having two hydrogen terminal groups. This could be explained by the chain-transfer reaction, as illustrated in Scheme 2, where the elimination of hydride anions from the propagating species and the reinitiation by the hydride anions occurred during the polymerization at 20°C. When the polymerization was carried out at −78°C, such molecular species arising from chain-transfer were not found as shown in Figure 4(c).

Figure 5 shows MALDI-ToF MS of polymers polymerized at 0°C with DPMK and DPMK/LiCl initiators. Multiple series of low molecular weight oligomer signals having different terminal groups were observed in the DPMK initiated polymers whereas only one series of signal attributable single polymer species was observed in the DPMK/LiCl system, indicating that the polymerization proceeded with lithium counter cations in the latter initiation system although the initial counter cation of the initiator was potassium.

As we have described before, the polymerization
mixture with potassium counter ions shows deep purple color at 0°C where chain-transfer occurred to some extent. Since the active chain end carbanion without chain-transfer appears pale yellow, this purple color might be related with deactivated polymer species or other type of anions. However, any anions that could be formed in this polymerization system should be quenched and rendered colorless by the addition of methanol, which actually did not occur. Therefore this color could have arisen from dead polymers having long conjugated systems whose structure is currently not clear.

**Microstructure of polyDEA**

Through the study of the diene polymerization, control and analysis of the microstructure of the polymer obtained is of considerable interest because the physical properties of the polydiene strongly depend on their microstructure. In this study, the microstructure of the resulting polymer was analyzed by $^1$H-NMR spectroscopy. Figure 6 shows the olefinic region of $^1$H-NMR spectra of polyDEA prepared by (a) free-radical polymerization, (b) anionic polymerization with DPMK initiators, (c) anionic polymerization with DPMK/LiCl initiators, and (d) anionic polymerization with Li-Naph.

![Scheme 2.](image)

![Figure 5.](image) MALDI-ToF MS spectra of polyDEA polymerized at 0°C for 24 h using DPMK and DPMK/LiCl initiators.

![Figure 6.](image) Olefinic region of $^1$H-NMR spectra of polyDEA prepared by (a) free-radical polymerization, (b) anionic polymerization with DPMK initiators, (c) anionic polymerization with DPMK/LiCl initiators, and (d) anionic polymerization with Li-Naph.

polymerization with DPMK/LiCl initiators, and (d) anionic polymerization with Li-Naph initiator.

As previously reported, 1,4-$E$ and 1,4-$Z$ structures of the main chain, respectively, were the main structures of polyDEA prepared by free-radical polymerization. The two olefinic signals centered at 5.35 and 5.23 ppm in Figure 5(a) can be assigned to protons in 1,4-$E$ and 1,4-$Z$ linkages, respectively. In addition to these signals, other olefinic proton signals around 5.1 and 6.1 ppm were observed in the polymer obtained by anionic polymerization. From the relative integrated intensity and
the C–H correlation spectroscopy (COSY) experiments, these signals are assigned to methylene and methine protons of 1,2-linkage, respectively. It is interesting that signals attributable to 1,4-Z linkage were not observed in the polymer obtained by DPMK initiated polymerization whereas both 1,4-E and Z linkages were incorporated in the DPMK/LiCl system. The ionic radii of the counterion might have affected the geometry of the monomer unit. In addition to this, no signals attributable to 3,4-linkage were observed. This indicates that the propagating anion derived from DEA always attacked to the C1 carbon of the butadienyl skeleton of DEA to form 1,4- or 1,2-anion as illustrated in Scheme 3. Table 2 summarizes the microstructure of the polymers prepared under various conditions. It is obvious that the microstructure of the resulting polymers was affected not only by the polymerization mechanism but also the kind of counter cations. In addition, polymers having almost the same microstructure were obtained in Li-Naph and DPMK/LiCl initiating systems regardless of the [LiCl]/[DPMK] ratio. One of the possibilities to explain this phenomenon might be a coordination of carboxyl group to lithium ion. In this case, excess amount of lithium ion could be coordinated not only by the active chain end but also by monomer and polymer chain, resulting in the difference of microstructure depends on the molar ratio of DPMK and LiCl, which is not compatible with the experimental result. Therefore most likely explanation is that cation exchange from potassium to lithium occurred in the DPMK/LiCl initiated polymerization mixture.

The formation of 1,2-linkage in the anionic polymerization provides important information on the reactivity of the active chain-end. As previously reported, almost no 1,2-linkage was formed in the free-radical polymerization of DEA, indicating that 1,2-radicals could not attack other monomers. The observation that a considerable amount of 1,2-structure was contained in the polymer obtained in this study indicates that the amide-enolate anion of the 1,2-propagating species has higher nucleophilic reactivity toward other monomer propagation resulting in the formation of 1,2-linkage in the polymer chain. However, the sequence distribution along the polymer chain is not clear yet.

Table 2. Microstructure of polyDEA Prepared under Various Conditions

| Mechanism  | Initiator     | [LiCl]/[DPMK] | Temperature (°C) | Microstructure (%) |
|------------|---------------|---------------|-----------------|--------------------|
|            |               |               |                 | 1,4-E 1,4-Z 1,2-2 3,4-3 |
| anionic    | DPMK          | —             | 78              | 50 0 50 0 |
|            | DPMK/LiCl     | 1.1           | 0               | 39 28 33 0 |
|            | DPMK/LiCl     | 5.3           | 0               | 37 30 33 0 |
|            | DPMK/LiCl     | 33.0          | 0               | 34 33 33 0 |
|            | Li-Naph       | —             | 0               | 36 32 32 0 |
| radical   | BPO/DMA       | —             | 5               | 34 64 2 |
|           | AIBN          | —             | 60              | 41 58 1 |
|           | 120c         | —             | 41 57 2 |

a) Ref. 7.
b) Benzoyl peroxide/N,N-dimethylaniline.
c) tert-Butyl peroxide.

Scheme 3.
Conclusion

Anionic polymerization of N,N-diethyl-2-methylene-3-butenanamide (DEA) was carried out in THF under various conditions. Polymers of predictable molecular weight with narrow molecular weight distributions were obtained when polymerization was carried out using lithium counter cations. Significant chain-transfer reactions occurred when potassium was used as a counter ion at sufficiently high polymerization temperatures. The microstructure of polymers prepared using potassium counter cations was a 1:1 mixture of 1,4-\(E\) and 1,2-structures. In the case of lithium counter ions, the microstructure was a complicated mixture of 1,4-\(E\), 1,4-\(Z\), and 1,2-structures.

Acknowledgement

This study was supported by a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1) Hshieh H. L. and Quirk R. P.: “Anionic Polymerization Principles and Practical Applications”, Marcel Dekker, New York, (1996)

2) Niu A. Z., Stellbrink J., Allgaier J., Willner L., Richter D., Koenig B. W., Gondorf M., Willbold S., Fetters L. J., May R. P.: “Proceedings of the 2003 International Symposium on Ionic Polymerization and Related Processes (Macromolecular Symposia 215)”, Ed. Mays J. W., Storey R. F., Wiley Interscience, New York, (2004), p. 1

3) Morton M.: “Anionic Polymerization: Principles and Practice”, Academic Press, New York, (1983)

4) Nishikawa M., Maeda M., Nakata H., Takamatsu H., Ishii M.: “Applications of Anionic Polymerization Research (ACS Symposium Series 696)”, Ed. Quirk R. P., American Chemical Society, Washington DC, (1998), p. 186

5) Sydnes L. K., Skattehol L.: Helv. Chim. Acta, 58, 2061 (1975)

6) Yaegashi T., Takeshita H., Takenaka K., Shioi T.: J. Polym. Sci., A Polym. Chem., 41, 1545 (2003)

7) Yaegashi T., Yodoya S., Nakamura M., Takeshita H., Takenaka K., Shioi T.: J. Polym. Sci., A Polym. Chem., 42, 999 (2004)

8) Xie X., Hogen-Esch T. E.: Macromolecules, 29, 1746 (1996)

9) Kobayashi M., Okuyama S., Ishizone T., Nakahama S.: Macromolecules, 32, 6466 (1999)

10) Ito M., Ishizone T.: J. Polym. Sci., A Polym. Chem., 44, 4832 (2006)

11) Alfrey T., Price C. C.: J. Polym. Sci., 2, 101 (1947)

12) Fayt R., Forte R., Jacobs C., Jerome R., Ouhadi T., Teyssie Ph., Varshney S. K.: Macromolecules, 20, 1442 (1987)

13) Varshney S. K., Hautekeer J. P., Fayt R., Jerome R., Teyssie Ph.: Macromolecules, 23, 2618 (1990)

14) Nakahama S., Kobayashi M., Ishizone T., Hirao A., Kobayashi M.: J. Macromol. Sci. Pure Appl. Chem., A34, 1845 (1997)