Polymerization of 1,3-Dienes with Functional Groups. 5.
RAFT Polymerization of $N,N$-diethyl-2-methylene-3-butenamide

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Abstract  Reversible addition-fragmentation chain transfer (RAFT) 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 chlorobenzene with using benzyl dithiobenzoate (BDB) as a chain transfer agent. When DEA was polymerized at 70°C using azobisisobutyronitrile (AIBN) as an initiator in the presence of BDB, polymers of narrow molecular weight distribution (Mw/Mn < 1.2) were obtained. The molecular weight increased proportionally with conversion, and the observed values were close to the calculated ones based on the molar ratio of monomer to BDB. This indicates that the molecular weight of the polymer can be controlled by the molar ratio of monomer to chain transfer agent. PolyDEA thus obtained contained BDB fragment which was confirmed by MALDI-TOF-MS analysis. Block copolymerization with styrene was carried out using polyDEA having BDB fragment as macro chain transfer agent. Microstructure of polyDEA was predominantly 1,4-structure. Thus simultaneous control of the molecular weight and microstructure was achieved in the RAFT polymerization of DEA.

Keywords  $N,N$-Diethyl-2-methylene-3-butenamide, RAFT polymerization, Microstructure, Benzyl dithiobenzoate, Block copolymerization.

Introduction

In the previous papers from our laboratory, we have reported the free-radical polymerization of $N,N$-diakyl-2-methylene-3-butenamides, 1,3-butadiene derivatives having dialkylamide function at the 2-position of butadienyl skeleton. By carefully choosing the polymerization condition, polymer of high 1,4-structure (>95%) was obtained in moderate yield without forming Diels-Alder dimmer or gels. However, the molecular weight distribution was relatively broad (Mw/Mn > 1.4) and the control of molecular weight was not easy.

On the other hand, it is well known that anionic polymerization of vinyl monomer is one of the best methods to prepare polymers having a well-characterized chain structure. Polydienes having high 1,4-microstructure can be obtained under appropriate conditions. In our previous report, we have reported the anionic polymerization behavior of $N,N$-diethyl-2-methylene-3-butenamide (DEA). Although the rate of polymerization is very slow, polymer of controlled molecular weight with narrow molecular weight distribution was obtained. The only problem in this anionic polymerization is the control of chain microstructure. When the polymerization was carried out in THF at -78°C with $K^+$ counter cation, polymer containing 50% 1,2- and 50% 1,4-E structure was obtained. If the polymerization was carried out with diphenylmethylpotassium/LiCl initiator or lithium naphthalenides, the microstructure comes to be a complex mixture of 1,4-E, 1,4-Z, and 1,2- linkage. From the viewpoint of microstructure control, free-radical polymerization is preferable though control of molecular weight and its distribution has some difficulty. In order to fulfill both requirements, living radical polymerization (LRP) would be the best solution.

In the past two decades, considerable effort has been expanded to develop free radical process that displays the characteristics of a living polymerization. Nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization are
the most representative controlled/living radical polymerization technologies. Although each technology has characteristics as summarized in a literature, we chose RAFT process for the polymerization of DEA because of its tolerant of a very wide range of functionality in the monomer. There have been some papers deals with the RAFT polymerization of 1,3-dienes. Perrrier et al. used trithiocarbonate compound and/or 2-(2-cyanopropyl) dithiobenzoate as RAFT agent for the polymerization of isoprene, though the molecular weight distribution was not so narrow (Mw/Mn=1.4)\(^{12}\). Ameduri et al. reported the RAFT polymerization of 1,3-butadiene using dithiobenzoate derivative containing perfluoroalkoxycarbonyl group at high temperature above 110°C \(^{13}\), which is not preferable for DEA to prevent the thermal polymerization. As we have reported previously, DEA has much higher polymerizability compared with those of conventional non-polar 1,3-dienes such as 1,3-butadiene and isoprene\(^ {23}\). Therefore ordinary benzyl dithiobenzoate (BDB), which does not contain any electron-withdrawing group that weakens the thioester linkage to enhance the polymerization, would be sufficient.

In this study, RAFT polymerization of DEA using BDB as RAFT agent was carried out, aiming the simultaneous control of molecular weight and microstructure of the resulting polymers.

**Experimental**

**Materials**

The synthetic procedure of DEA has been described elsewhere\(^ {23}\). It was stirred for 12 h with calcium hydride, and was distilled under reduced pressure. Styrene was washed with aqueous sodium hydroxide to remove inhibitor followed by water. After drying with anhydrous sodium sulfate, it was distilled under reduced pressure in the presence of calcium hydride. BDB was synthesized by the reaction of phenylmagnesium bromide with carbon disulfide followed by the addition of benzyl bromide\(^ {14}\). AIBN was recrystallized from methanol. Chlorobenzene was distilled under reduced pressure in the presence of calcium hydride.

**RAFT polymerization**

All the polymerizations were carried out in a sealed glass ampoules. In a typical case, 1.00 g (6.5 mmol) of DEA, 0.0317 g (0.13 mmol) of BDB, 8.84 mg (0.0654 mmol) of AIBN were weighed in a 5 mL volumetric flask and diluted with chlorobenzene. Then it was transferred to glass ampoule and was degassed three times by freeze-pump-thaw method and finally sealed under vacuum. Then the ampoule was put in a temperature controlled oil bath and stirred for designed polymerization time. After polymerization, small amount of the reaction mixture was withdrawn for NMR analysis, and the aliquot was poured into \(n\)-hexane 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.

**Block copolymerization with styrene**

A 0.7631 g of polyDEA containing BDB fragment (Mn=9700), 15.8 mg of AIBN, and 2.0 g of styrene are weighed in glass ampoule and diluted with small amount of benzene. It was degassed three times by freeze-pump-thaw method and finally sealed under vacuum. Then the ampoule was put in an oil bath preheated at 70°C and stirred for 5 h. After polymerization, the reaction mixture was poured into \(n\)-hexane 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 NMR spectrum was recorded using a JEOL JNM-AL-400 spectrometer in CDCl\(_3\) or DMSO-\(d_6\). A solvent peak was used as a reference. Size exclusion chromatography (SEC) chromatogram was obtained at 40°C using a TOSOH HLC-8220 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 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-RR 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

RAFT polymerization of DEA

Choice of RAFT agents is of considerable importance for the better control of molecular weight and its distribution of the resulting polymers. Various kinds of RAFT agents were synthesized and used for the polymerization of vinyl monomers\(^{10}\). However, little has been reported for the RAFT polymerization of diene monomers. RAFT polymerization of 1,3-butadiene and isoprene in the presence of fluorinated dithiobenzoates\(^{13}\) and trithiocarbonates\(^{12}\), respectively, were reported, though they are not commonly used RAFT agents. As we have mentioned previously, it is possible to regard DEA as \(\alpha\)-vinyl-\(N,N\)-dialkylacrylamides\(^{1,2}\). RAFT polymerization of \(N,N\)-dialkylacrylamides was studied extensively by several groups. For example, BDB was employed for the synthesis of hydrophilic-hydrophobic block copolymer having a low polydispersity, in which RAFT polymerization of styrene was conducted in the presence of BDB, followed by the polymerization of \(N,N\)-dimethylacrylamide\(^{15}\). This indicates that BDB can be used as RAFT agents for the polymerization of vinyl monomers having wide variety of reactivity. We selected BDB for this reason.

When red-colored chlorobenzene solution of DEA, BDB, and AIBN was heated in a sealed glass tube, gradual increase of viscosity was observed with time. After reprecipitation, pale pink-colored polymer was obtained. Figure 1 shows the \(^1\)H-NMR spectra of the polymerization mixture. It is obvious that the relative integrated intensity of the signal at 6.4 ppm, which is attributable to olefinic methine proton in the monomer, decreased by polymerization. It was possible to determine the conversion by comparing the signal intensity of the olefinic signal at 6.4 ppm with that of methyl protons at 1.05 ppm because the ethyl group on amide nitrogen atom does not change its intensity regardless of the conversion and the microstructure of the resulting polymers.

Figure 2 shows the MALDI-ToF MS spectrum of the resulting polymers. As can be seen, two series of signals having 153 Da intervals corresponding to the polymer molecules having different degrees of polymerization were observed. Since the mass differences between each signals in the two groups are approximately 22, these signals could be attributed to the polymer fragments having different adduct ions, \([M+Na]^+\) or \([M+H]^+\), or polymer fragments having different chain-end structure.

According to the well-known RAFT polymerization mechanism, each polymer molecule should have RAFT agent fragment at polymer chain-end as shown in Scheme 2. In this study, this was confirmed by comparing the molecular mass of the polymer fragment with that of the calculated one based on the above-mentioned mechanism. For example, molecular mass of the \(i\)-mer of DEA having BDB fragment at the chain-end can be expressed as

\[
M_i = 153.12i + 244.04
\]
where 153.12 and 244.04 are exact molar mass of DEA and BDB, respectively. In the case of Na⁺ adduct of 23-mer, the calculated molecular mass comes to 3788.8, which agreed well with the observed value 3788.72. On the other hand, we have to pay attention that two series of signals were observed in the MALDI-ToF-MS analysis. If i-mer initiated with isobutyronitrile group and terminated by hydrogen abstraction reaction exists in the sample, molar mass of the i-mer comes to

\[ M_i = 153.12i + 69.06 = 153.12(i-1) + 222.18 \] (2)

where 69.06 indicates the sum molar mass of isobutyronitrile group and hydrogen. As can be seen, molar mass difference between i-mer with BDB fragments and (i+1)-mer of isobutyronitrile fragment comes to approximately 22, suggesting that polymer samples obtained in this study may contain polymers without BDB fragment at the polymer chain-end. This will be discussed in detail concerning the block copolymerization with styrene.

Table 1 summarizes the result of RAFT polymerization at 70°C using BDB and AIBN as RAFT agent and initiator, respectively. When DEA, BDB and AIBN are charged in the molar ratio of 100 : 2 : 1, molecular weights measured by SEC increased proportionally with conversion, and their distributions were kept narrow throughout the polymerization. (Mw/Mn<1.2) The number average molecular weights estimated using polystyrene calibration were close to the calculated ones based on the amount of consumed DEA to BDB ratio. These results indicate that well controlled polymerization proceeded under the conditions employed here compared with the previously reported AIBN initiated polymerization of DEA where Mw/Mn value was larger than 1.5.

Figure 3 shows the SEC chromatograms of polyDEA by RAFT polymerization with different polymerization time. As can be seen, each chromatogram shifted to higher molecular weight side with time keeping its distribution unimodal and narrow in the early stage of polymerization. This indicates that no apparent termination reaction occurred during this period and that the BDB

![Figure 3. SEC chromatograms of polyDEA by RAFT polymerization with different polymerization time.](image)

| DEA (g) | BDB (mmol) | AIBN (mmol) | [DEA]/[BDB] | [DEA]/[AIBN] | Time (h) | Conv. (%) | Mn (kg/mol) | Mw/Mn | SEC |
|---------|------------|-------------|-------------|-------------|----------|-----------|-------------|-------|-----|
| 1.00    | 6.53       | 32.1        | 0.131       | 10.8        | 0.066    | 50        | 99          | 1     | 19.6| 1700 | 1300 | 1.16 |
| 1.00    | 6.53       | 32.2        | 0.132       | 10.8        | 0.066    | 50        | 99          | 2     | 29.8| 2500 | 2000 | 1.18 |
| 1.00    | 6.53       | 32.2        | 0.132       | 10.8        | 0.066    | 50        | 99          | 5     | 52.1| 4200 | 3100 | 1.17 |
| 1.00    | 6.53       | 32.0        | 0.131       | 10.8        | 0.066    | 50        | 99          | 10    | 73.6| 5900 | 4600 | 1.17 |
| 1.00    | 6.53       | 32.2        | 0.132       | 10.7        | 0.065    | 50        | 100         | 15    | 85.4| 6700 | 4910 | 1.18 |
| 1.00    | 6.53       | 32.2        | 0.132       | 10.5        | 0.064    | 50        | 100         | 20    | 93.6| 7300 | 5800 | 1.18 |
| 1.00    | 6.53       | 64.0        | 0.262       | 21.4        | 0.130    | 25        | 50          | 15    | 95.5| 3900 | 4110 | 1.19 |
| 1.00    | 6.53       | 32.2        | 0.132       | 10.7        | 0.065    | 50        | 100         | 15    | 85.4| 6700 | 4910 | 1.18 |
| 1.00    | 6.53       | 21.3        | 0.087       | 7.15        | 0.044    | 75        | 150         | 15    | 81.6| 9600 | 7900 | 1.15 |
| 1.00    | 6.53       | 16.0        | 0.065       | 5.35        | 0.033    | 100       | 200         | 15    | 80.2| 12500| 9130 | 1.20 |

![Figure 4. MALDI-ToF-MS spectrum of polyDEA measured by using reflector mode.](image)
fragment attached to polymer chain end effectively acted as RAFT agent as long as enough amount of monomer present in the polymerization mixture. At the late stage of polymerization where most of the monomer was consumed, small shoulder peak presumably due to the coupling of the polymer chain came to be clear.

In order to check the possibility of such a side reaction, low molecular weight polyDEA prepared with BDB : AIBN : DEA = 2 : 1 : 50 was analyzed by MALDI-ToF-MS using reflector mode which makes it possible to obtain mass spectrum with higher resolution in the oligomer region. Figure 4 shows MALDI-ToF-MS chart of the polymers, where at least 5 series of signals having 153 Da intervals were observed. It should be noted that each of the signals attributable to the polymer molecules having almost the same molar mass shows multiple signals. This cannot be explained simply by the existence of isotopic signals such as \([M+1]^+\) or \([M+2]^+\), suggesting that polymer species having different chain-end structure coexists in the sample. By comparing the molar mass of

| Code           | Polymer Structure | Termination mode    |
|----------------|-------------------|---------------------|
| IB-(DEA)n-H    | ![IB-(DEA)n-H](https://example.com/ib-dean-h.png) | Disproportionation  |
| IB-(DEA)n-C=C  | ![IB-(DEA)n-C=C](https://example.com/ib-dean-c-c.png) |                     |
| BN-(DEA)n-Bn   | ![BN-(DEA)n-Bn](https://example.com/bn-dean-bn.png) | Recombination       |
| BN-(DEA)n-DB   | ![BN-(DEA)n-DB](https://example.com/bn-dean-db.png) | RAFT                |
| BN-(DEA)n-H    | ![BN-(DEA)n-H](https://example.com/bn-dean-h.png) | Disproportionation  |
| BN-(DEA)n-C=C  | ![BN-(DEA)n-C=C](https://example.com/bn-dean-c-c.png) |                     |
| DA-(DEA)n-H    | ![DA-(DEA)n-H](https://example.com/da-dean-h.png) | Disproportionation  |
| DA-(DEA)n-C=C  | ![DA-(DEA)n-C=C](https://example.com/da-dean-c-c.png) |                     |

- **Diels-Alder Reaction**: Plausible thermal initiation mechanism via Diels-Alder reaction

**Scheme 3.**
the polymer having plausible chain-end structure as illustrated in Scheme 3 with the observed ones, assignment of each signal in Figure 4 was carried out and summarized in Table 2. Table 2 summarizes the observed molar mass and the calculated ones based on the possible polymer molecules having different chain-end structure. Although variety of polymer species could be assigned to each series of the signals, there seems to be no doubt that the polymer species that does not contain dithiobenzoate fragments formed by recombination of propagating radicals and/or disproportionation exist in the sample, though their signal intensities are not so high. Of course it is obvious that these kind of termination reaction should not be major reaction in the polymerization conditions employed here, otherwise the molecular weight distribution would have become much broader. However, we should be careful for the possibility that certain amount of polymer species without BDB fragment might be contained in the sample.

**Block copolymerization with styrene**

One of the most important features of controlled radical polymerization (CRP) is the advantage for the synthesis of block copolymers. Since BDB fragment attached to the chain end of polyDEA is expected to be act as polymeric RAFT agent, block copolymerization with styrene as second monomer was attempted. Figure 5 shows SEC chromatograms of the polyDEA precursor and the block copolymers obtained. It is obvious that elution curve of the block copolymer shifted higher molecular weight side, although certain amount of polymer seemed to remain at

| Table 2 | Molar mass of the polymer fragments having different chain-end structures |
|---------|--------------------------------------------------------------------------------------------------|
| \( m/z \text{ (obsd)} \) | \( \text{Bn-(DEA)}_n \text{-Bn} \) | \( \text{IBN-(DEA)}_n \) | \( \text{IBN-(DEA)}_n \) | \( \text{Bn-(DEA)}_n \) | \( \text{Bn-(DEA)}_n \) | \( \text{DA-(DEA)}_n \) | \( \text{DA-(DEA)}_n \) |
| Na⁺ | Na⁺ | Na⁺ | Na⁺ | Na⁺ | H⁺ | Na⁺ | Na⁺ | Na⁺ | Na⁺ |
| 817.88 | 1011.07 | 1032.06 | 1066.07 | 1093.09 |
| 857.93 | 1010.77 | 1016.65 | 1030.77 | 1031.76 |
| 878.94 | 1018.75 | 1032.63 | 1035.63 | 1037.63 |
| 912.95 | 940.71 | 939.69 | 1009.83 | 1009.81 |
| 939.97 | 970.03 | 971.03 | 1010.85 | 1010.83 |
| 971.03 | 1010.77 | 1016.65 | 1030.77 | 1031.76 |
| 1011.07 | 1032.06 | 1035.63 | 1037.63 | 1039.69 |
| 1032.06 | 1035.63 | 1037.63 | 1039.69 | 1041.76 |
| 1123.10 | 1123.82 | 1123.82 | 1123.82 | 1123.82 |
| 1162.22 | 1163.89 | 1163.89 | 1163.89 | 1163.89 |
| 1187.18 | 1185.75 | 1185.75 | 1185.75 | 1185.75 |
| 1215.16 | 1186.89 | 1186.89 | 1186.89 | 1186.89 |
| 1246.33 | 1184.88 | 1184.88 | 1184.88 | 1184.88 |
| 1276.94 | 1183.83 | 1183.83 | 1183.83 | 1183.83 |
| 1315.37 | 1317.01 | 1317.01 | 1317.01 | 1317.01 |
| 1338.37 | 1340.01 | 1340.01 | 1340.01 | 1340.01 |
| 1398.37 | 1388.87 | 1388.87 | 1388.87 | 1388.87 |
| 1533.19 | 1535.19 | 1535.19 | 1535.19 | 1535.19 |
| 1552.17 | 1554.17 | 1554.17 | 1554.17 | 1554.17 |
| 1645.62 | 1646.25 | 1646.25 | 1646.25 | 1646.25 |
| 1678.58 | 1687.11 | 1687.11 | 1687.11 | 1687.11 |
| 1707.51 | 1705.29 | 1705.29 | 1705.29 | 1705.29 | 1705.29 | 1705.29 |

Bn: benzyl, IBN: iso-butynitrile, H: saturated group, C=C: unsaturated group, DA: Diels–Alder dimeric group. For detail, see Scheme 3.

\( \text{Na⁺} \): Unknown polymer fragments.
the original position. This indicates that some part of the polyDEA precursor acted as macro RAFT agent to give block copolymer composed of polar polyDEA segment and non-polar polystyrene segment. Block copolymer formation of this sequence is of practical importance. In our previous paper, we have reported the anionic polymerization of DEA under various conditions. Anionic polymerization of DEA could be initiated by weak nucleophile such as diphenylmethyl potassium, indicating that the anionic polymerizability of DEA is much higher than that of styrene. In other words, nucleophilicity of active chain end carbanion derived from DEA is too weak to initiate the polymerization of styrene. As a consequence, polySt-polyDEA-polySt type of triblock copolymer could not easily be obtained by anionic polymerization whereas polyDEA-polySt-polyDEA can be prepared simply by the sequential addition of the monomers. Our result obtained in this study showed the possibility to overcome the above-mentioned limitation. On the other hand, we have to pay attention that the block efficiency was not high enough in this study. As mentioned above, certain amount of polyDEA was kept unchanged after block copolymerization. PolyDEA without BDB fragment in the polymer could be responsible for the lowering of block efficiency.

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 polydienes strongly depend on their microstructure. In this study, the microstructure of the resulting polymer was analyzed by 1H-NMR spectroscopy. Figure 6 shows the olefinic region of 1H-NMR spectra of polyDEA prepared by (a) conventional free-radical polymerization, (b) RAFT polymerization, (c) anionic polymerization with K⁺ counter ion, and (d) anionic polymerization with Li⁺ counter ion.

As previously reported, 1,4-E and Z linkage, cis- and trans-1,4 structures of the main chain, respectively, were the main structures of polyDEA prepared by conventional free-radical polymerization. The two olefinic signals centered at 5.35 and 5.23 ppm in Figure 6(a) can be assigned to protons in 1,4-E and 1,4-Z linkages, respectively. No apparent difference was observed for the RAFT polymer shown in Figure 6(b). This indicates RAFT agent fragment does not interfere the monomer addition to the propagating species. On the other hand, additional olefinic proton signals around 5.1 and 6.1 ppm were observed in the polymer obtained by anionic polymerization as illustrated in Figure 6(c) and (d). 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. Thus the microstructure of polyDEA prepared by anionic polymerization was found to be a complex mixture of 1,4-E, 1,4-Z, and 1,2-linkage.

Table 3 summarizes the microstructure of the polymers prepared under various conditions. It is obvious that the microstructure of the polymers obtained by RAFT polymerization was almost the same as that prepared by conventional free-radical polymerization. Thus highly 1,4-
Poly(DEA) with controlled molecular weight was obtained.

**Conclusion**

RAFT polymerization of N,N-diethyl-2-methylene-3-butenamide (DEA) was carried out in chlorobenzene using benzyl dithiobenzoate (BDB) as RAFT agent. Molecular weight of the polymers was controllable by adjusting the molar ratio of BDB and DEA. Molecular weight distributions of the polymers were relatively narrow (Mw/Mn<1.2). The microstructure of polymers was mainly (>95%) 1,4-linkage, which was completely different from the result of anionic polymerization but was similar to the results by conventional free radical polymerization. By using RAFT process, simultaneous control of molecular weight and microstructure was achieved.

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**References and Notes**

1) Yeagashi T., Takeshita H., Takenaka K., Shiomi T.: *J. Polym. Sci. A. Polym. Chem.*, 41, 1545 (2003).
2) Yeagashi T., Yodoya S., Nakamura M., Takeshita H., Takenaka K., Shiomi T.: *J. Polym. Sci. A. Polym. Chem.*, 42, 999 (2004).
3) Hsien H. L., Quirk R. P.: “Anionic Polymerization: Principles and Practical Applications”, Marcel Dekker, New York, (1996).
4) 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 Volume 215), Ed. Mays J. W., Storey R. F., Wiley Interscience, (2004), p. 1.
5) Morton M.: “Anionic Polymerization: Principles and Practice”, Academic Press, New York, (1983).
6) 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 D.C., (1999), p. 186.
7) Takenaka K., Shibata N., Tsuchida S., Takeshita H., Miya M., Shiomi T.; e-J. Soft Mater., 4, 23 (2008).
8) Moad G., Solomon G. H.: “The Chemistry of Radical Polymerization (second fully revised edition)”, Elsevier, Oxford, (2006), p. 451.
9) Matyjaszewski K., Davis T. P. (Eds.), “Handbook of Radical Polymerization”, Wiley-Interscience, New York, (2002), p. 361.
10) Barner-Kowollik C. (Ed.), “Handbook of RAFT Polymerization”, Wiley-VCH, Weinheim, (2008).
11) Matyjaszewski K., Davis T. P. (Eds.), “Handbook of Radical Polymerization”, Wiley-Interscience, New York, (2002), p. 397.
12) Jitchum V., Perrier S.: *Macromolecules*, 40, 1408 (2007).
13) Lebreton P., Ameduri B., Boutevin B., Corpart J.-M.: *Macromol. Chem. Phys.*, 203, 522 (2002).
14) Chong Y. K., Kristna J., Le T. P. T., Moad G., Postma A., Rizzardo E., Thang S. H.: *Macromolecules*, 36, 2256 (2003).
15) Chong Y. K., Le T. P. T., Moad G., Rizzardo E., Thang S. H.: *Macromolecules*, 32, 2071 (1999).
16) Takenaka K.: Unpublished result. Although poly(DEA) was obtained in moderate yield at 80°C, molecular weight and its distribution could not be controlled.

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Table 3. Microstructure of polyDEA prepared under various conditions

| Mechanism | Initiator | Temp. (°C) | Microstructure (%) |
|-----------|-----------|------------|--------------------|
|           |           |            | 1,4-E | 1,4-Z | 1,2-Z |
| anionic   | DPMK      | −78        | 50    | 0     | 50    |
|           | DPMK/LiCl | 0          | 34    | 33    | 33    |
|           | Li-Naph   | 0          | 36    | 32    | 32    |
| radical   | BPO/DMA   | 5          | 34    | 64    | 2     |
|           | AIBN      | 60         | 41    | 58    | 1     |
|           | ‘BPO’     | 120        | 42    | 57    | 1     |
| RAFT      | AIBN      | 70         | 44    | 53    | 3     |
| ATRP      | EIMP/Ru(II) | 80     | 42    | 56    | 2     |

a) Ref. 7.
b) Diphenylmethylpotassium.
c) Lithium naphthalenide.
d) Ref. 2.
e) Benzoyl peroxide/N,N-dimethylaniline.
f) tert-Butyl peroxide.
g) Ref. 16.
h) Ethyl 2-iodo-2-methylpropanoate/RuCl₃(PPh₃).