

Development of Stereospecific Living Radical Polymerization with UV-LED Irradiation

by

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Abstract

Effect of simple alkyl alcohol on radical polymerization of *N*-isopropylacrylamide (NIPAAm) in toluene at low temperatures was investigated. We succeeded in inducing syndiotactic-specificity and accelerating polymerization reaction at the same time by adding simple alkyl alcohols into NIPAAm polymerization. Furthermore, effect of chain transfer agent on NIPAAm polymerization at low temperatures was also examined. Living nature was observed with use of LED as UV light source even for the low-temperature radical polymerization.

Key words: *N*-isopropylacrylamide, Radical Polymerization, Stereoregularity, Living Polymerization

1. Introduction

Porter and coworkers^(1, 2) have reported preparation of highly isotactic polymers by radical polymerization of acrylamide derivatives, in which chiral groups, such as chiral oxazolidine, were employed as stereocontrolling auxiliaries. Okamoto and coworkers^(3, 4) have reported condition-controlled isotactic-specific radical polymerization of acrylamide derivatives, in which catalytic amounts of Lewis acids, such as yttrium trifluoromethanesulfonate, were employed as stereocontrolling auxiliaries. The both polymerization systems provided isotactic polymers with *meso* (*m*) dyad content over 90%. Thus, the isotactic-specificity in radical polymerization of acrylamide derivatives has been successfully achieved.

On the other hand, preparation of highly syndiotactic polymers by radical polymerization of acrylamide derivatives had been hardly reported, except for the following systems; (1) a syndiotactic polymer with *racemo* (*r*) dyad content of 93% (*N,N*-diphenylacrylamide in tetrahydrofuran at -98°C),⁽⁵⁾ (2) a syndiotactic polymer with *r* dyad content of 76% (3-acryloyl-2-oxazolidinone in toluene at -78°C).⁽⁶⁾ The syndiotacticity of the former is comparable to those of polymers obtained via anionic polymerizations of *N,N*-disubstituted acrylamides.^(7, 8) The stereochemistry, however, strongly depends on the structure of the monomers.^(5, 9) For example, *N,N*-dimethylacrylamide provided isotactic polymers under the corresponding polymerization conditions. Thus, the development of condition-controlled syndiotactic-specific radical polymerization of acrylamide derivatives has been strongly desired.

Recently, we have found that a hydrogen-bonding interaction between *N*-isopropylacrylamide (NIPAAm) and Lewis base is

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useful for controlling stereospecificity of radical polymerization of NIPAAm.⁽¹⁰⁻¹²⁾ The hydrogen-bond-induced stereospecificity depended on polymerization conditions such as the kind of the added Lewis base and the solvent. Isotactic poly(NIPAAm) with *m* dyad content of 74% was obtained at -60°C in 1:1 (vol/vol) mixed solvent of chloroform and CH₃CN in the presence of 3,5-dimethylpyridine *N*-oxide.⁽¹²⁾ Syndiotactic poly(NIPAAm)s were obtained in toluene in the presence of phosphoric acid derivatives.^(10, 11) In particular, by adding an excess amount of hexamethylphosphoramide (HMPA), the dyad syndiotacticity of the obtained poly(NIPAAm)s reached up to 72% that is the highest syndiotacticity among those of the radically prepared poly(NIPAAm)s.⁽¹⁰⁾ Thus, we made the first step to fulfill the above-mentioned desire. However, this polymerization requires careful operation, because of the toxicity of HMPA. So, as the next target, we focused our interest on the development of syndiotactic-specific polymerization induced by safer reagents instead of HMPA.

It is known that alcohol compounds play efficient roles in controlling stereospecificity of

radical polymerization of vinyl monomers.⁽¹³⁻¹⁶⁾ In particular, fluoroalcohol compounds, such as 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and perfluoro-*t*-butanol, exhibit significant stereoregulating power in radical polymerization of ester monomers such as vinyl esters⁽¹³⁾ and methacrylates.^(14, 15) Recently, we also found that not only HFIP but also simple alkyl alcohols such as *t*-butanol (*t*-BuOH) significantly decreased syndiotactic-specificity in radical polymerization of *N*-vinylacetamide (NVA),⁽¹⁶⁾ although simple alkyl alcohols hardly affected the stereospecificity in the polymerization of vinyl esters and methacrylates. This is probably because Lewis basicity of carbonyl group of amide group in NVA is stronger than those of ester monomers. Thus, we started investigating the effect of simple alkyl alcohols on the stereospecificity in radical polymerization of NIPAAm,⁽¹⁷⁾ which is also one of monomers containing amide group as well as NVA.

Recently, controlled radical polymerizations, such as atom transfer radical polymerization,^(18, 19) nitroxide-mediated radical polymerization,⁽²⁰⁾ and reversible addition-fragmentation chain transfer (RAFT) polymerization,^(21, 22) have been investigated

Table 1. Radical polymerization of NIPAAm in toluene for 24h at various temperatures in the absence or presence of a fourfold amount of simple alcohols^a

Run	Alcohol	Temp. °C	Yield %	Tacticity / % ^b		M_n^c x 10 ⁻⁴	M_w^c M_n
				<i>m</i>	<i>r</i>		
1 ^d	None	-40	89	46	54	2.72	1.8
2	MeOH	-40	98	38	62	2.44	1.3
3	EtOH	-40	86	36	64	3.76	1.3
4	<i>i</i> -PrOH	-40	92	36	64	2.87	1.3
5	<i>t</i> -BuOH	-40	99	33	67	4.01	1.5
6	3Me3PeOH	-40	>99	31	69	5.88	1.5
7 ^e	None	0	55	47	53	5.85	2.4
8 ^e	3Me3PenOH	0	94	35	65	6.87	2.1

a. [NIPAAm]₀ = 0.5 mol/L, [R-OH]₀ = 2.0 mol/L, [*n*-Bu₃B]₀ = 0.05 mol/L.

b. Determined by ¹H NMR signals due to methylene group.

c. Determined by SEC (polystyrene standards).

d. Monomer, polymer or both were precipitated during a polymerization reaction.

e. [*n*-Bu₃B]₀ = 0.01 mol/L, polymerization time 10min.

extensively to synthesize polymers with controlled molecular weight and narrow molecular weight distribution. Among them, RAFT has been successfully applied for controlling radical polymerization of NIPAAm.⁽²³⁻²⁶⁾ However, the polymerization was usually carried out at elevated temperatures. Thus, we attempted the use of UV-LED as a light source to control RAFT photopolymerization of NIPAAm at low temperatures.

2. Results and Discussion

2.1 Radical polymerization of NIPAAm at low temperatures in the presence of alcohol

First, we carried out radical polymerization of NIPAAm in toluene at -40°C in the presence of a fourfold amount of alkyl alcohol compounds, such as methanol (MeOH), ethanol (EtOH), isopropanol (*i*-PrOH), *t*-butanol (*t*-BuOH), and 3-methyl-3-pentanol (3Me3PenOH), to investigate the effect of alcohol compounds on the stereospecificity of NIPAAm polymerization (Table 1). Adding alkyl alcohols significantly induced syndiotactic-specificity, and the magnitude was enhanced with the bulkiness of the added alcohols. This result indicates that alkyl alcohols have an

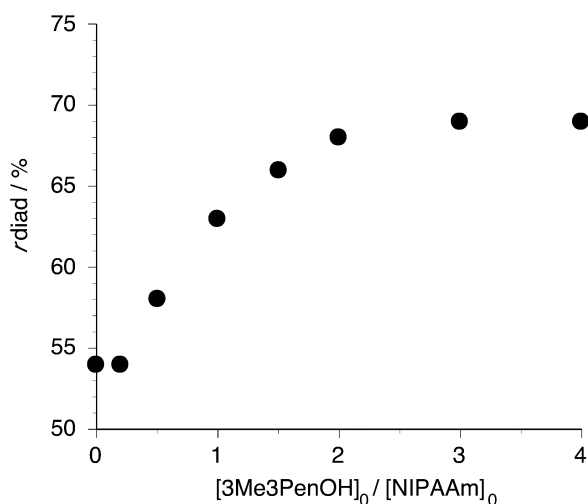


Figure 1. Relationship between the $[\text{3Me3PenOH}]_0 / [\text{NIPAAm}]_0$ ratio and the r dyad content of poly(NIPAAm)s obtained.

efficient stereocontrolling power in the radical polymerization of NIPAAm as well as NVA. It should be noted that the added alkyl alcohols induced opposite stereospecificity in the polymerization of NVA and NIPAAm.

Next, we examined effect of the added amount of alcohol compounds on the syndiotactic-specificity in NIPAAm polymerization at -40°C . Figure 1 demonstrates relationship between the $[\text{3Me3PenOH}]_0 / [\text{NIPAAm}]_0$ ratio and r dyad content of the obtained poly(NIPAAm)s. The syndiotacticity gradually increased with the $[\text{3Me3PenOH}]_0 / [\text{NIPAAm}]_0$ ratio and became almost constant over the ratio = 2, whereas the addition of catalytic amount of 3Me3PenOH hardly influenced the stereospecificity. This result suggests that at least a twofold amount of alcohols is required in order to significantly induce the syndiotactic-specificity in this polymerization system.

It has been reported that, in radical polymerization of NIPAAm in water, an increase in $[\text{M}]_0$ results in a decrease in apparent propagation rate coefficient (k_p), probably due to strong aggregation of monomers and/or polymers.⁽²⁷⁾ Although both Lewis bases and alcohol compounds should dissociate such aggregations, polymers were quantitatively obtained in the presence of alcohols and, on the contrary, an obvious retardation was observed in the presence of HMPA. This result suggests that hydrogen-bond-assisted complex formation also changed the reactivity of NIPAAm monomer. Based on the quantitative yield in the presence of alcohol compounds, it is assumed that alcohol compounds accelerate the polymerization reaction. Thus, we examined the acceleration effect of alcohol compounds by reducing initiator concentration (0.01 mol/L) and shortening polymerization time (10min) at 0°C (Table 1, Runs 7 and 8). The both polymerization systems proceeded homogeneously and the polymer yield pronouncedly increased by adding 3Me3PenOH, as expected.

2.2 RAFT photopolymerization of NIPAAm at

low temperatures

RAFT polymerization of NIPAAm was carried out in toluene at -20°C in the presence of $i\text{PrOH}$. High-pressure mercury lamp was used as a light source. S -1-Dodecyl- S' -(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (DDMAT) and 2,4,6-trimethylbenzoyldiphenylphosphine oxide

(TMDPO) were used as a chain transfer agent and an initiator, respectively.⁽²⁸⁻³⁰⁾ The polymer yield proportionally increased with the polymerization time (Figure 2). Furthermore, roughly linear increase in molecular weight with the polymer yield was observed with narrow molecular weight distribution (Figure 3). These results suggest that the

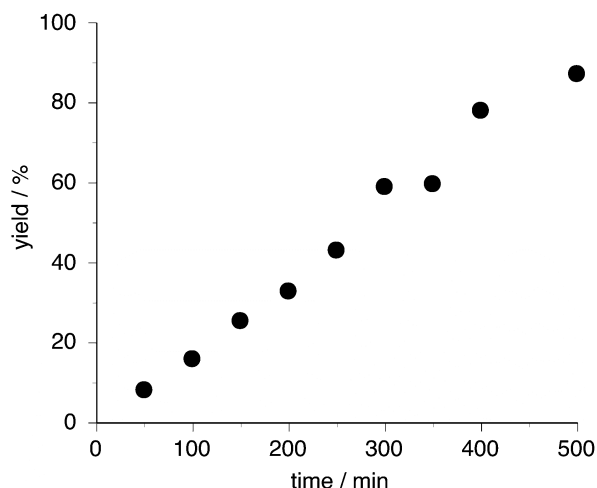


Figure 2. Relationship between the polymerization time and the polymer yield for the RAFT polymerization of NIPAAm initiated by TMDPO with high-pressure mercury lamp irradiation.

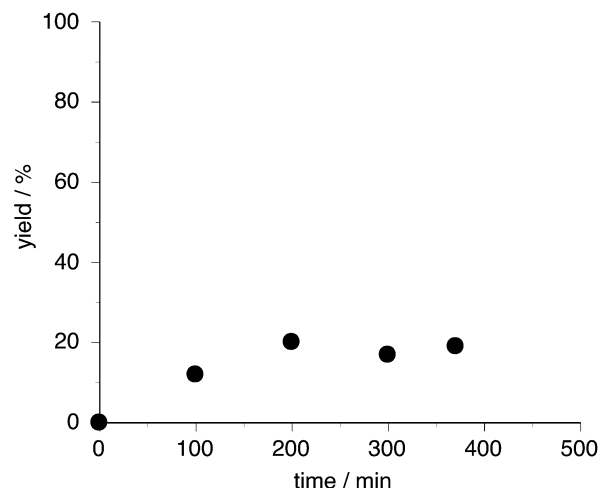


Figure 4. Relationship between the polymerization time and the polymer yield for the RAFT polymerization of NIPAAm initiated by TMDPO with UV-LED irradiation.

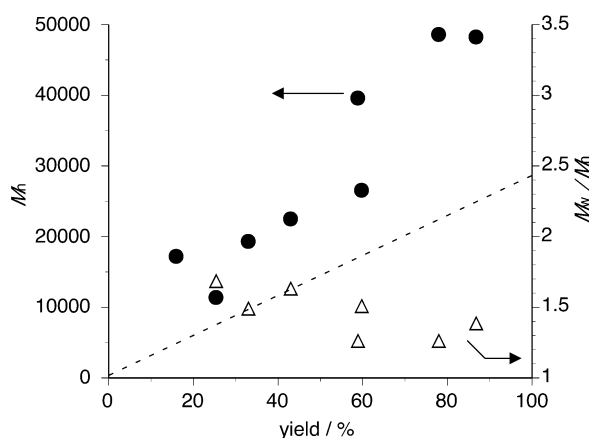


Figure 3. Relationship between the yield and the molecular weight (distribution) of the polymers obtained by the RAFT polymerization of NIPAAm initiated by TMDPO with high-pressure mercury lamp irradiation.

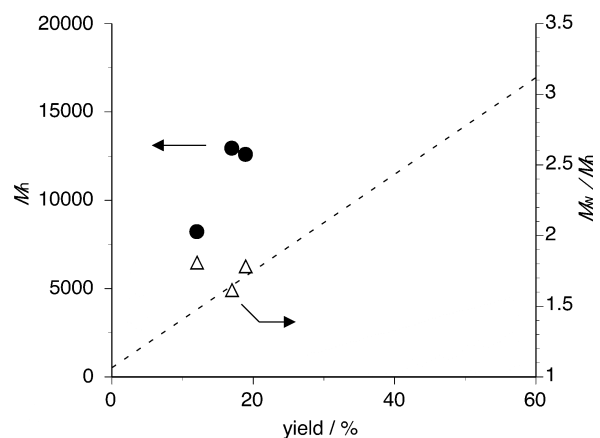


Figure 5. Relationship between the yield and the molecular weight (distribution) of the polymers obtained by the RAFT polymerization of NIPAAm initiated by TMDPO with UV-LED irradiation.

polymerization proceeded in a living/controlled manner.

Then, UV-LED was used as a light source instead of high-pressure mercury lamp. The polymer yield reached plateau after 200 min of initiation (Figure 4). Moreover, molecular weight and molecular weight distribution of the polymers

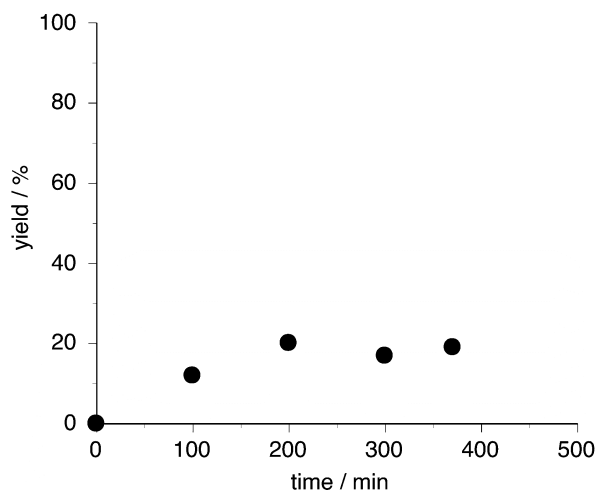


Figure 6. Relationship between the polymerization time and the polymer yield for the RAFT polymerization of NIPAAm initiated by MAIB with UV-LED irradiation.

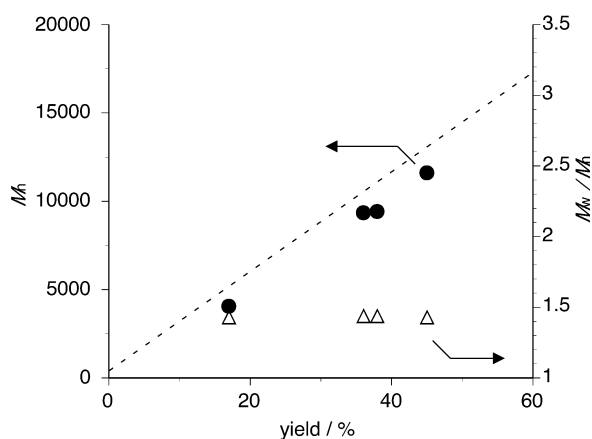


Figure 7. Relationship between the yield and the molecular weight (distribution) of the polymers obtained by the RAFT polymerization of NIPAAm initiated by MAIB with UV-LED irradiation.

obtained were hardly controlled (Figure 5).

Thus, dimethyl 2,2'-azobisisobutyrate (MAIB) was used as an initiator instead of TMDPO. The polymer yield proportionally increased with the polymerization time, although the yield was much lower than when high-pressure mercury lamp was used (Figure 6). Furthermore, linear increase in molecular weight with the polymer yield was also observed with narrow molecular weight distribution (Figure 7), indicating that UV-LED can be used as a better light source for the low-temperature living/controlled radical photopolymerization of NIPAAm as expected.

3. Conclusion

Radical photopolymerization of NIPAAm in toluene at low temperatures was investigated in the presence of chain transfer agent and alcohols. Simultaneous control of tacticity and molecular weight was successfully achieved with the use of UV-LED as a light source.

Acknowledgements

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References

1. N. A. Porter, T. R. Allen, R. A. Breyer: Chiral auxiliary control of tacticity in free radical polymerization. *J Am Chem Soc*, 114(20), 7676-7683 (1992).
2. W.-X. Wu, A. T. McPhail, N. A. Porter: Polymerization and Telomerization of Chiral Acrylamides. *The Journal of Organic Chemistry*, 59(6), 1302-1308 (1994).
3. Y. Isobe, D. Fujioka, S. Habaue, Y. Okamoto: Efficient Lewis Acid-Catalyzed Stereocontrolled Radical Polymerization of Acrylamides. *J Am Chem Soc*, 123(29), 7180-7181 (2001).
4. S. Habaue, Y. Isobe, Y. Okamoto: Stereocontrolled radical polymerization of acrylamides and methacrylamides using Lewis acids. *Tetrahedron*, 58(41), 8205-8209 (2002).

5. W. Liu, T. Nakano, Y. Okamoto: Stereocontrol in Radical Polymerization of N,N-Dimethylacrylamide and N,N-Diphenylacrylamide and Thermal Properties of Syndiotactic Poly(methyl acrylate)s Derived from the Obtained Polymers. *Polym J*, 32(9), 771-777 (2000).
6. C. L. Mero, N. A. Porter: Free-Radical Polymerization and Copolymerization of Acrylimides: Homopolymers of Oxazolidinone Acrylimide and Control of 1,5-Stereochemistry in Copolymers Derived from Isobutylene and an Oxazolidinone Acrylimide. *The Journal of Organic Chemistry*, 65(3), 775-781 (2000).
7. M. Kobayashi, S. Okuyama, T. Ishizone, S. Nakahama: Stereospecific Anionic Polymerization of N,N-Dialkylacrylamides. *Macromolecules*, 32(20), 6466-6477 (1999).
8. M. Kobayashi, T. Ishizone, S. Nakahama: Additive Effect of Triethylborane on Anionic Polymerization of N,N-Dimethylacrylamide and N,N-Diethylacrylamide. *Macromolecules*, 33(12), 4411-4416 (2000).
9. T. Hirano, S. Nasu, A. Morikami, K. Ute: The effect of the N-substituent s-trans to the carbonyl group of N-methylacrylamide derivatives on the stereospecificity of radical polymerizations. *J Polym Sci, Part A: Polym Chem*, 47(23), 6534-6539 (2009).
10. T. Hirano, H. Miki, M. Seno, T. Sato: Effect of polymerization conditions on the syndiotactic-specificity in radical polymerization of N-isopropylacrylamide and fractionation of the obtained polymer according to the stereoregularity. *Polymer*, 46(15), 5501-5505 (2005).
11. T. Hirano, S. Ishii, H. Kitajima, M. Seno, T. Sato: Hydrogen-bond-assisted stereocontrol in the radical polymerization of N-isopropylacrylamide with primary alkyl phosphate: The effect of the chain length of the straight ester group. *J Polym Sci, Part A: Polym Chem*, 43(1), 50-62 (2005).
12. T. Hirano, H. Ishizu, R. Yamaoka, K. Ute, T. Sato: Metal-free isotactic-specific radical polymerization of N-alkylacrylamides with 3,5-dimethylpyridine N-oxide: The effect of the N-substituent and solvent on the isotactic specificity. *Polymer*, 50(15), 3522-3527 (2009).
13. K. Yamada, T. Nakano, Y. Okamoto: Stereospecific Free Radical Polymerization of Vinyl Esters Using Fluoroalcohols as Solvents. *Macromolecules*, 31(22), 7598-7605 (1998).
14. Y. Isobe, K. Yamada, T. Nakano, Y. Okamoto: Stereospecific Free-Radical Polymerization of Methacrylates Using Fluoroalcohols as Solvents. *Macromolecules*, 32(18), 5979-5981 (1999).
15. Y. Isobe, K. Yamada, T. Nakano, Y. Okamoto: Stereocontrol in the free-radical polymerization of methacrylates with fluoroalcohols. *J Polym Sci, Part A: Polym Chem*, 38(S1), 4693-4703 (2000).
16. T. Hirano, Y. Okumura, M. Seno, T. Sato: Remarkable effect of hydrogen-bonding interaction on stereospecificity in the radical polymerization of N-vinylacetamide. *Eur Polym J*, 42(9), 2114-2124 (2006).
17. T. Hirano, Y. Okumura, H. Kitajima, M. Seno, T. Sato: Dual roles of alkyl alcohols as syndiotactic-specificity inducers and accelerators in the radical polymerization of N-isopropylacrylamide and some properties of syndiotactic poly(N-isopropylacrylamide). *J Polym Sci, Part A: Polym Chem*, 44(15), 4450-4460 (2006).
18. K. Matyjaszewski, J. Xia: Atom Transfer Radical Polymerization. *Chem Rev*, 101(9), 2921-2990 (2001).
19. M. Kamigaito, T. Ando, M. Sawamoto: Metal-Catalyzed Living Radical Polymerization. *Chem Rev*, 101(12), 3689-3746 (2001).
20. C. J. Hawker, A. W. Bosman, E. Harth: New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations. *Chem Rev*, 101(12), 3661-3688 (2001).
21. J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang: Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process. *Macromolecules*, 31(16), 5559-5562 (1998).

22. G. Moad, E. Rizzardo, S. H. Thang: Living Radical Polymerization by the RAFT Process. *Aust J Chem*, 58(6), 379-410 (2005).
23. F. Ganachaud, M. J. Monteiro, R. G. Gilbert, M.-A. Dourges, S. H. Thang, E. Rizzardo: Molecular Weight Characterization of Poly(N-isopropylacrylamide) Prepared by Living Free-Radical Polymerization. *Macromolecules*, 33(18), 6738-6745 (2000).
24. C. Schilli, M. G. Lanzendorfer, A. H. E. Muller: Benzyl and Cumyl Dithiocarbamates as Chain Transfer Agents in the RAFT Polymerization of N-Isopropylacrylamide. In Situ FT-NIR and MALDI-TOF MS Investigation. *Macromolecules*, 35(18), 6819-6827 (2002).
25. B. Ray, Y. Isobe, K. Morioka, S. Habaue, Y. Okamoto, M. Kamigaito, M. Sawamoto: Synthesis of Isotactic Poly(N-isopropylacrylamide) by RAFT Polymerization in the Presence of Lewis Acid. *Macromolecules*, 36(3), 543-545 (2003).
26. B. Ray, Y. Isobe, K. Matsumoto, S. Habaue, Y. Okamoto, M. Kamigaito, M. Sawamoto: RAFT Polymerization of N-Isopropylacrylamide in the Absence and Presence of Y(OTf)₃: Simultaneous Control of Molecular Weight and Tacticity. *Macromolecules*, 37(5), 1702-1710 (2004).
27. F. Ganachaud, R. Balic, M. J. Monteiro, R. G. Gilbert: Propagation Rate Coefficient of Poly(N-isopropylacrylamide) in Water below Its Lower Critical Solution Temperature. *Macromolecules*, 33(23), 8589-8596 (2000).
28. L. Lu, N. Yang, Y. Cai: Well-controlled reversible addition-fragmentation chain transfer radical polymerisation under ultraviolet radiation at ambient temperature. *Chem Commun*(42), 5287-5288 (2005).
29. H. Zhang, J. Deng, L. Lu, Y. Cai: Ambient-Temperature RAFT Polymerization of Styrene and Its Functional Derivatives under Mild Long-Wave UV-vis Radiation. *Macromolecules*, 40(26), 9252-9261 (2007).
30. L. Lu, H. Zhang, N. Yang, Y. Cai: Toward Rapid and Well-Controlled Ambient Temperature RAFT Polymerization under UV-Vis Radiation: Effect of Radiation Wave Range. *Macromolecules*, 39(11), 3770-3776 (2006).