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Stereospecific Polymerization of α-Substituted Acrylates

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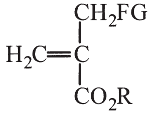
SUMMARY: α-Substituted acrylates having various functional groups, such as alkoxymethyl, aminomethyl and alkylthiomethyl groups, on the α-position were synthesized and polymerized by radical and anionic methods, and stereoregularity of the obtained polymers was investigated. In the anionic polymerization using lithium reagents, highly isotactic polymers were obtained regardless of the polarity of solvents. Strong intra- and intermolecular coordination of the polar groups to counter-cation (Li^+) may be the main factor in controlling the stereochemistry. On the other hand, stereocontrol in the radical polymerization of α-(alkoxymethyl)acrylates was attained in the presence of zinc salts ($ZnBr_2$ and $ZnCl_2$), which may coordinate to the growing polymer and monomers.

Introduction

Design and stereospecific synthesis of polymers possessing a variety of functional groups are an attractive and important area in polymer science. α-Substituted acrylates are the monomers that have two different types of substituents on an olefin. Effects of polar groups on the reactivity and stereoregulation in anionic polymerization are of great interest from the view points of the intra- and intermolecular coordination to a counter-cation by the functional groups, and successful design of these groups can provide a useful method for the control of higher order structure, as well as the stereoregularity.



$$H_2C{=}\overset{\displaystyle CH_2FG}{\underset{\displaystyle CO_2R}{C}}$$

FG: functional group

Results and Discussion

Stereospecific Anionic Polymerization of α-(Alkoxymethyl)acrylate

Although atactic polymers have been obtained in the radical polymerization of α-(alkoxymethyl)acrylates, little data are available about the tacticity of the anionic

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polymerization[1 - 3]. Thus, the anionic polymerization of benzyl α-(methoxymethyl)acrylate (**BMMA**) using lithium reagents was investigated[4]. The polymerization with alkyllithium at –78°C proceeded moderately, giving poly(**BMMA**) in 20 – 77% yields, while the radical polymerization with (i-PrOCO$_2$)$_2$ in toluene at 30°C afforded a polymer quantitatively.

In ^{1}H NMR spectra of the poly(**BMMA**)s obtained by the radical and anionic polymerizations in toluene (Fig. 1), the spectral pattern of the main chain methylene protons shows a typical AB quartet with a coupling constant 15.0 Hz for the latter polymer, indicating that the poly(**BMMA**) obtained by the anionic polymerization in toluene possesses a high isotacticity, while the polymer obtained by the radical method may be atactic. Fig. 2 shows the ^{13}C NMR spectra of the carbonyl carbon of poly(**BMMA**)s. A sharp peak is observed for the poly(**BMMA**) anionically prepared (Fig. 2(b)), and multi-peaks for the polymer obtained by the radical method (Fig. 2(a)). This observation also supports that the anionic polymerization of BMMA in toluene proceeds in a highly isotactic-specific manner. It is noteworthy that the polymers produced with a lithium reagent in THF showed a sharp peak assigned to highly isotactic sequences (Fig. 2(c)). This result is in marked contrast to that of the anionic polymerization of α-(alkyl)acrylates, which usually affords the polymers rich in syndiotacticity in THF[5 - 7].

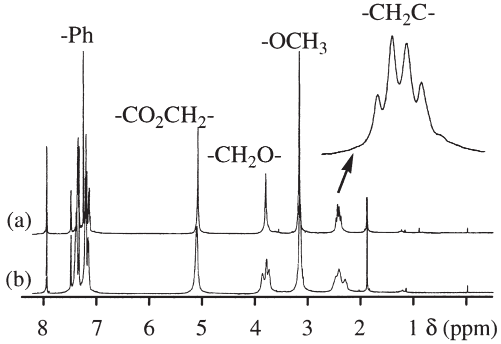


Fig. 1: ^{1}H NMR spectra of poly(**BMMA**)s obtained with t-BuLi in toluene at –78°C (a) and with a radical initiator at 30°C (b) (nitrobenzene-d_5, 110°C).

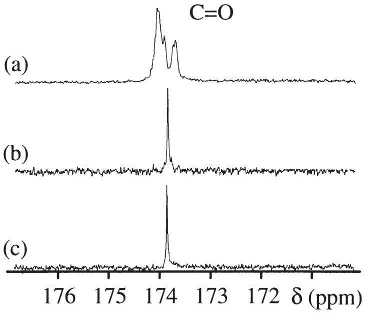
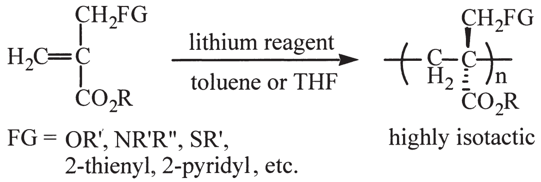
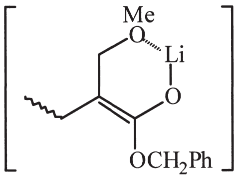


Fig. 2: ^{13}C NMR spectra of poly(**BMMA**)s obtained with a radical initiator at 30°C (a), with t-BuLi in toluene (b) and with t-BuLi in THF (c) (CDCl$_3$, 60°C).

The anionic polymerization of α-substituted acrylates having various functional groups, such as alkoxymethyl, N,N-dialkylaminomethyl, 2-thienylmethyl and 2-pyridylmethyl groups, with lithium reagents proceeds in a highly isotactic-specific manner regardless of the polarity of solvents similarly to the anionic polymerization of **BMMA**[8 - 13]. Strong intra- and intermolecular coordination of the polar groups of the growing polymer chain and monomers to the counter-cation (Li^+), especially, a stable six-membered chelation of intermediate lithium enolate, should be the main factor in controlling the stereochemistry.



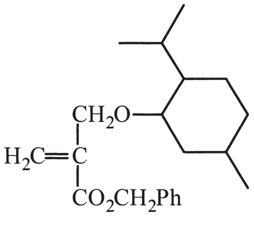


Stereospecific Polymerization of Chiral α-(Alkoxymethyl)acrylate

In the anionic polymerization of acrylate derivatives, introduction of a functional group on the α-position may be a novel method for the control of the higher order structure, in addition to the stereoregularity. A regular arrangement of successfully designed optically active groups along an isotactic polymer chain should form a chiral helical conformation[14, 15].

α-(Alkoxymethyl)acrylates bearing a chiral substituent, racemic and optically active benzyl α-(menthoxymethyl)acrylates ((±)- and (–)-**BMnMA**), were synthesized and polymerized by radical and anionic methods. The radical polymerization of **BMnMA** gave atactic polymers regardless of the chirality of the monomer, while the anionic polymerization of optically pure (–)-**BMnMA** and probably (±)-**BMnMA** provided highly isotactic polymers. The polymers prepared from optically pure (–)-monomer with an anionic initiator (the complexe of *N,N'*-diphenylethylenediamine monolithium amide (DPEDALi) with *N,N,N',N'*-tetramethylethylenediamine (TMEDA)) had low solubility in common organic solvents. The THF-soluble parts exhibited much lower specific rotation ($[\alpha]_{365}^{25} = -92°$: degree of polymerization (DP) = 16, Mw / Mn = 1.4) than those of the monomer ($[\alpha]_{365}^{25} = -226°$) and the radically obtained polymer ($[\alpha]_{365}^{25} = -201°$: DP = 14, Mw / Mn = 1.5).

The circular dichroism (CD) spectra of (–)-**BMnMA** and poly((–)-**BMnMA**)s obtained by radical and anionic methods are demonstrated in Fig. 3. Both CD spectra of the monomer (Fig. 3(a)) and radically obtained polymer (Fig. 3(b)) showed the negative cotton effect, which may be due to an isolated (–)-menthyl ether group, indicating that the optical activity of the radically obtained polymer is mainly based on that of each menthyl ether group on the side chain. The CD pattern of the anionically obtained polymer (Fig. 3(c)) was quite different from those of the monomer and the radically prepared polymer. In addition to a large positive cotton effect at 210 nm and a small one at 230 nm, peaks around 260 nm, which may be due to phenyl group were clearly observed. This indicates that a new chirality due to a regular arrangement of ether groups, probably a helical conformation of a polymer chain, is induced for the anionically obtained highly isotactic polymer. The lower specific rotation of the anionically prepared polymer arises from the compensation between the competing cotton effects of menthyl ether group and the helical structure.



BMnMA

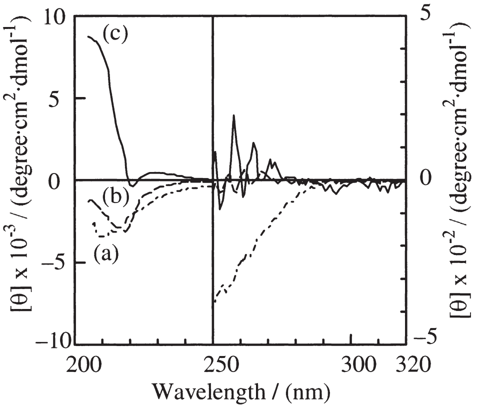


Fig. 3: CD spectra of the monomer, (–)-**BMnMA** (a), poly((–)-**BMnMA**) obtained with (i-$PrOCO_2)_2$ (b) and with DPEDA-TMEDA (c) (THF, r.t.).

The results of the anionic copolymerization of mixtures of (+)- and (–)-**BMnMA** initiated with DPEDALi-TMEDA complex are shown in Table 1. The copolymerization proceeded in a good yield in every case, and the solubility of the obtained copolymers decreased with an increase of enantiomeric excess (e.e.) of the charged monomer. Interestingly, non-linear relationship between the specific rotation of the copolymers and % e.e. of the charged monomer is clearly observed and the specific rotations reached a plateau value around 60 % e.e.. These results again suggest that the isotactic (–)-**BMnMA** sequence has a conformation that can contribute to the optical activity of the polymer chain.

Table 1. Anionic copolymerization of (+)- and (–)-**BMnMA** with DPEDALi-TMEDA complex in toluene[a]

% e.e. of (–)-**BMnMA**	Yield (%)[b]	THF-soluble part Yield (%)	DP[c,d]	Mw/Mn[d]	$[\alpha]^{25}_{365}$[e]
0	89	100	20	1.32	—
20	92	100	14	1.49	–46°
40	90	100	15	1.74	–82°
60	79	100	15	1.85	–89°
80	95	80	16	1.55	–91°
100	94	16	16	1.38	–92°

[a] [monomer]/[initiator] = 20, temp. –78°C, time 24h.

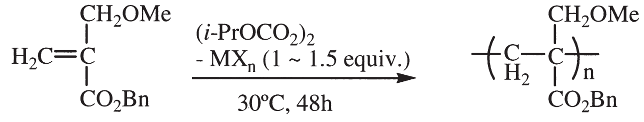
[b] Methanol-insoluble part. [c] Degree of polymerization.

[d] Determined by SEC (polystyrene standard).

[e] In THF (c = 0.5).

Stereocontrol in Radical Polymerization of α-(Alkoxymethyl)acrylates

Stereocontrol in the radical polymerization of vinyl monomers is a most important goal in synthetic polymer chemistry. Although numerous works have reported on stereospecific polymerization based on anionic and coordination mechanisms, little is known concerning the stereocontrol in radical method[16 - 19]. Stereocontrol in radical polymerization using BMMA as a monomer in the presence of various metal salts, which may coordinate growing polymer and monomers, was investigated[20].



$$H_2C{=}C(CH_2OMe)(CO_2Bn) \xrightarrow[30^\circ C,\ 48h]{(i\text{-}PrOCO_2)_2\ -\ MX_n\ (1 \sim 1.5\ equiv.)} \left[CH_2{-}C(CH_2OMe)(CO_2Bn) \right]_n$$

BMMA poly(**BMMA**)

Fig. 4(b) shows the ^{1}H NMR spectrum of the main chain methylene protons of poly(**BMMA**) obtained by radical polymerization in the presence of $ZnBr_2$ in CH_2Cl_2, together with those of the polymers prepared without $ZnBr_2$ in CH_2Cl_2 (c) and with n-BuLi in toluene at –78°C (m > 99%)[4] (c) for comparison. The spectral pattern of the polymer obtained in the presence of $ZnBr_2$ is quite different from that prepared without a salt, indicating that some stereocontrol takes place in the radical polymerization with $ZnBr_2$. While little change was observed on the stereoregularity of the polymers obtained with LiCl and $MgCl_2$, the polymerization using zinc salts ($ZnCl_2$ and $ZnBr_2$) gave the polymers having different tacticity from that prepared in the absence of metal salt. However, a polar solvent, THF, greatly reduced the effect of the stereocontrol by $ZnBr_2$ judging from the spectral pattern of ^1H NMR, suggesting that the coordination of zinc salts to the growing polymer and the monomer is important in this system.

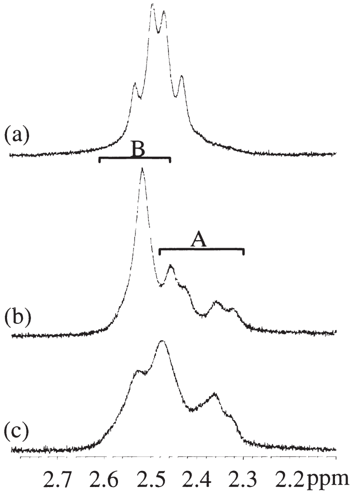


Fig. 4: ^1H NMR spectra of the main chain methylene protons in poly(**BMMA**) obtained with *n*-BuLi in toluene at –78°C (a), with radical method in the presence of $ZnBr_2$ in CH_2Cl_2 (b) (nitrobenzene-d_5, 110°C) and without $ZnBr_2$ (c) (nitrobenzene-d_5, 150°C).

In Fig. 4(b), the four peaks in the area A seem assignable to an AB quartet with a coupling constant of about 16 Hz due to the diastereotopic *meso*-protons. Therefore, a peak in the region B may be due to the protons of *racemo*-diad. However, since the chemical shifts for the former four peaks are different from those for the protons of the *isotactic*-poly(BMMA), the higher order (tetrad) tacticity should be considered the spectral pattern for the main chain methylene protons of poly(**BMMA**). Supposing that the peaks from 2.3 to 2.4 ppm are ascribed to one of the protons of *meso*-diad, diad tacticity of the polymer prepared using

$ZnBr_2$ is estimated to be *r* : *m* = 67 : 33, while that of the radically obtained polymer in its absence is nearly r ≈ m (≈ 0.5). The diad tacticities of the poly(**BMMA**) prepared in the presence of $ZnBr_2$ in toluene was evaluated to be *r* : *m* = 70 : 30.

The addition of zinc chloride accelerates the polymerization rate of methacrylates,21) and tacticity is hardly changed during the polymerization, while an increase of isotacticity was observed in radical bulk polymerization of the complexes of methacrylate with zinc chloride.22 - 24) The radical polymerization of benzyl methacrylate (**BnMA**) with $ZnBr_2$ was also carried out by the same procedure as that for the polymerization of **BMMA**. The polymer was obtained using $ZnBr_2$ (1.5 equiv.) in CH_2Cl_2 in 97% yield (DP = 59, Mw / Mn = 2.0) with a triad tacticity, *mm* : *mr* : *rr* = 3 : 34 : 63, while poly(**BnMA**) (96% yield, DP = 120, Mw / Mn = 4.8) prepared in its absence showed a tacticity, 3 : 33 : 64. These results indicate that the zinc salts characteristically affect the stereoregularity of poly(**BMMA**) in the radical polymerization, and a polar α-substituent on an acrylate is important in the stereocontrol of this system.

Conclusion

Stereospecific anionic and radical polymerizations of α-substituted acrylates having various functional groups, such as alkoxymethyl, aminomethyl and alkylthiomethyl groups, on the α-position were attained. In the anionic polymerization using lithium reagents, highly isotactic polymers were obtained regardless of the polarity of solvents. Strong intra- and intermolecular coordination of the polar groups to counter-cation (Li^+) for anionic polymerization or zinc salts for radical method should be the main factor in controlling the stereochemistry. New functional polymers with a variety of functional groups arranged on the main chain of a stereoregular polyacrylate were synthesized.

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