SHORT COMMUNICATIONS

An Extraordinary Effect of Ether on the Polymerization of Methacrylates with Grignard Reagent in Toluene

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Many papers have been published on the polymerization of methacrylates by Grignard reagents. In these polymerization systems, there exist independent active centers of different reactivities and stereospecificities, whose proportions depend on the reaction conditions.¹⁻⁶ The polymers usually become more syndiotactic as the ether component of the solvent mixture increases.^{1-3,5} A highly isotactic polymer was formed in toluene on using de-etherated C_6H_5MgBr or $t-C_4H_9MgBr$ as an initiator.^{4,7} This clearly indicates that the active center solvated with ether molecule is syndiotactic-favoring and the unsolvated center is isotactic-favoring.³⁾

In this work, it was found that the de-etherated C_4H_9MgCl or C_4H_9MgBr gave a highly syndiotactic poly(methyl methacrylate) (PMMA) in toluene, while a mixture of isotactic and syndiotactic polymers was formed in toluene in the presence of diethyl ether. An extraordinary effect of de-etheration was also observed in the polymerization of ethyl, isopropyl, and *t*-butyl methacrylates with C_4H_9MgCl . The formation of a mixture of isotactic and syndiotactic PMMAs with C_4H_9MgCl has already been reported by Inagaki and his coworkers.⁸

Butylmagnesium halides were prepared in diethyl ether from the corresponding butyl halide and magnesium. The concentration of Grignard reagent thus obtained was adjusted to 0.86 mol l^{-1} , and the solution was used as the initiator, which is described as "BuMgX/Et₂O" (X = Cl or Br).

The de-etheration of BuMgX/Et₂O was carried out by evaporating the solution under high vacuum, followed by redissolving the residue in toluene and evaporating the solvent again. The resulting white powder was suspended in toluene and used as the "de-etherated BuMgX." The powder dissolved completely in tetrahydrofuran-*d*₈ and the ¹H NMR spectrum of the solution indicated that the mole ratio of Et₂O : BuMgX was 0.10 : 1.0 for de-etherated BuMgCl and 0.15 : 1.0 for de-etherated BuMgBr. In further experiments, the white powder was redissolved in Et₂O. The titration of this solution by *s*-butanol, using 9,10-phenanthroline as an indicator⁹ confirmed that most of the BuMg-groups were active (>99%). Also, the NMR spectrum was identical to that of BuMgX/Et₂O. The polymerizations of MMA and EMA by the BuMgCl/Et₂O, prepared from the de-etherated BuMgCl by the addition of Et₂O, brought about essentially the same results as when using the original BuMgCl/Et₂O (*cf.* Tables I and II). Thus, an irreversible change does not occur during the de-etheration procedure.

Polymerization was initiated by adding the monomer slowly to the initiator solution cooled to the polymerization temperature. The reaction vessel was then sealed off. The reaction was terminated by the addition of a small amount of methanol at the reaction temperature. Isolation of the polymer and oligomer was carried out as reported previously.¹⁰

Polymerization of methyl methacrylate (MMA)

Table I. Polymerization of MMA with Grignard reagent in toluene at -78°C for 24 h^a

Initiator	Polymer					Oligomer
	Yield	Tacticity/%			M_n^c	
		%	I	H		
BuMgCl/Et ₂ O	49 ^b	31	21	48	17600	18
BuMgCl/Et ₂ O ^d	1	10	15	75	—	16
De-etherated BuMgCl	87	3	19	78	54700	11
BuMgCl/Et ₂ O ^e	59	32	16	52	—	28
BuMgBr/Et ₂ O ^g	6	32	12	56	—	12
De-etherated BuMgBr ^g	90	4	21	75	—	10
<i>t</i> -BuMgCl/Et ₂ O ^g	41	68	9	23	—	59
De-etherated <i>t</i> -BuMgCl ^{f,g}	34	23	16	61	—	3

^a Monomer, 10 mmol; solvent, 10 ml; initiator, 1.0 mmol.^b By using a competitive adsorption method,⁸ the polymer was separated into isotactic (46%) and syndiotactic (54%) fractions, with tacticities of I:H:S=62:13:25 and I:H:S=11:24:65, respectively.^c Determined by GPC calibrating the chromatogram against standard polystyrene samples.^d Polymerization in THF.^e The initiator used in this run was prepared by the addition of a small amount of Et₂O to the de-etherated BuMgCl (Et₂O: BuMgCl=10:1).^f The de-etheration of *t*-BuMgCl/Et₂O was unsuccessful by the procedure described in the text (Et₂O: *t*-BuMgCl=0.64:1.0). Consequently the de-etheration of *t*-BuMgCl was carried out by evacuation at 100°C for 5 h (Et₂O: *t*-BuMgCl=0.05:1.0).^g Initiator 0.5 mmol.**Table II.** Polymerization of ethyl methacrylate with BuMgCl in toluene at -78°C for 24 h^a

Initiator	MeOH-soluble part					MeOH-insoluble part				
	Yield %	Tacticity/%			M_n^b	Yield %	Tacticity/%			M_n^b
		I	H	S			I	H	S	
BuMgCl/Et ₂ O	52 ^c	100	0	0	11700	0	—	—	—	—
De-etherated BuMgCl	48	16	34	50	9400	50	0	26	74	73800
BuMgCl/Et ₂ O ^d	60	100	0	0	—	0	—	—	—	—

^a Monomer, 10 mmol; solvent, 10 ml; initiator, 1.0 mmol.^b Determined by GPC.^c The polymer consisted of hexane-soluble (9%) and -insoluble (91%) parts.^d The initiator used in this run (0.5 mmol) was prepared by the addition of a small amount of Et₂O to the de-etherated BuMgCl (Et₂O: BuMgCl=10:1).

with BuMgCl/Et₂O and de-etherated BuMgCl were carried out in toluene at -78°C . The results are shown in Table I. Polymerization by BuMgCl/Et₂O gave a mixture of isotactic and syndiotactic polymers and methanol-soluble oligomer as reported by Inagaki *et al.*⁸ When the de-etherated BuMgCl

was used as the initiator, a highly syndiotactic polymer was formed in high yield and the oligomer decreased in amount. This indicates that the amount of initiator consumed for the formation of polymer and oligomer decreased on using the de-etherated initiator. However, the rate of polymerization was

higher with the de-etherated BuMgCl than by the BuMgCl/Et₂O initiator. Therefore, the activity of de-etherated BuMgCl should be higher than that of BuMgCl/Et₂O. The ether component is of importance in determining the kinetics and stereospecificity of polymerization with the Grignard reagent; however, it usually enhances the formation of the syndiotactic polymer.^{1-3,5} Polymerization with BuMgCl/Et₂O in THF gave a syndiotactic polymer and an oligomer (Table I). In view of this the increase in the syndiotacticity upon the de-etheration is an unexpected phenomenon. A similar effect of de-etheration was observed on the polymerization of MMA with BuMgBr and *t*-BuMgCl, as shown in Table I.

The results of the polymerization of ethyl methacrylate (EMA) with BuMgCl in toluene at -78°C are shown in Table II. PEMA obtained by BuMgCl/Et₂O was completely soluble in methanol. When the polymer was fractionated by hexane, a highly isotactic and high molecular weight polymer was obtained as an insoluble fraction and an isotactic oligomer as a soluble fraction. Polymerization with the de-etherated initiator formed methanol-soluble and -insoluble fractions. Both fractions were found to be syndiotactic and the syndiotacticity of insoluble fraction was higher than that of soluble one. Formation of an isotactic polymer by BuMgCl/Et₂O and a syndiotactic polymer by de-etherated BuMgCl was also observed in the polymerization of isopropyl and *t*-butyl methacrylates.¹¹ These results indicate that the formation of a syndiotactic polymer by de-etherated Grignard reagent is a general trend in the polymerization of methacrylate.

The electron spin resonance (ESR) spectrum of the de-etherated BuMgCl-MMA system showed 9 ($=5+4$) lines ($a=24$ gauss, 24 gauss), quite similar to that of the MMA propagating radical.¹² The signal was observed even at 0°C , indicating a higher

stability of the radical. The BuMgCl/Et₂O-MMA system showed no ESR signals. Therefore, there is some possibility of a radical or coordinated radical mechanism for polymerization with the de-etherated initiator. However, such a radical mechanism should not be of great importance, since the radical concentration was estimated to be $1 \times 10^{-8} \text{ mol l}^{-1}$ at most. An extensive study is now under way along with an NMR study on the structure of the initiators, and the results will be published in the near future.

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