spectra of **1a** and **1b** showed no abnormality which may arise from their intermolecular aggregation.

The present study demonstrates a novel, intramolecular cooperation of otherwise weak Brønsted base and Lewis acid in the bifunctional activation of a simple ketone under mild conditions. The efficient cooperation arises from a rigid steric restraint imposed on the basic and metal centers, which forces them in proximity but prevents their direct interaction. The present finding is significant for the development of catalytic organic reactions under neutral and mild conditions since so many organic reactions are subject to catalysis by acid and base, and the concerted acid–base catalysis is one of the general mechanisms by which the enzymes catalyze biological reactions.

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Novel Photoinduced Carbon–Carbon Bond Formation via Metal–Alkyl and –Enolate Porphyrins—Visible Light-Mediated Polymerization of Alkyl Methacrylate Catalyzed by Aluminum Porphyrin

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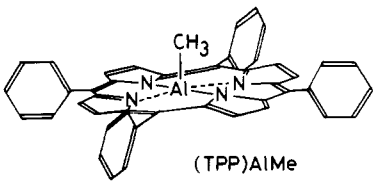
Photocatalysis with metalloporphyrin has been studied mainly in connection with biological photosynthesis. Electron transfer from excited metalloporphyrin to an acceptor resulting in charge separation, eventually leading to hydrogen evolution from water, has been the subject of much interest.[1] In the present communication, we report an unprecedented type of the photocatalysis with metalloporphyrin, in which the formation of carbon–carbon bonds proceeds by the effect of visible light. The reaction is the polymerization of alkyl methacrylate catalyzed by (tetraphenylporphinato)aluminum methyl ((TPP)AlMe)[2] upon irradiation with visible light to give a polymer of narrow molecular weight distribution.



(TPP)AlMe

For example, to a 50-cm^3 flask containing 0.4 mmol of (TPP)AlMe (16-cm^3 CH_2Cl_2 solution) was added 100-fold of methyl methacrylate (4.3 cm^3) through a three-way stopcock by a syringe in dry nitrogen atmosphere. The flask was illuminated by a 300-W xenon arc lamp from a distance of 25 cm through a glass filter to cut out light of wavelength shorter than 420 nm and thermostated at 30 °C. Within an hour the reaction mixture turned from bluish purple to brownish purple. After 12 h, an excess of methanol was added, and the volatile materials were removed under reduced pressure to leave the product, which was identified as poly(methyl methacrylate) by ^{13}C NMR.[3] The polymer could be separated from the residual catalyst by dissolving the product in acetone followed by filtration.

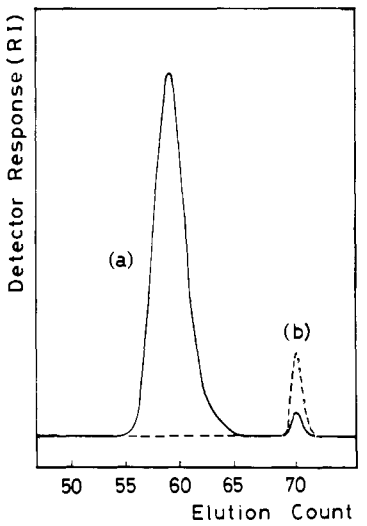


Figure 1. GPC profile (in THF) of the reaction mixture of methyl methacrylate with (TPP)AlMe (100/1). Reaction in benzene, 30 °C, 13 h: (a) upon irradiation, conversion = 43%, $\bar{M}n$ = 3960, $\bar{M}w/\bar{M}n$ = 1.19 and (b) in the dark.

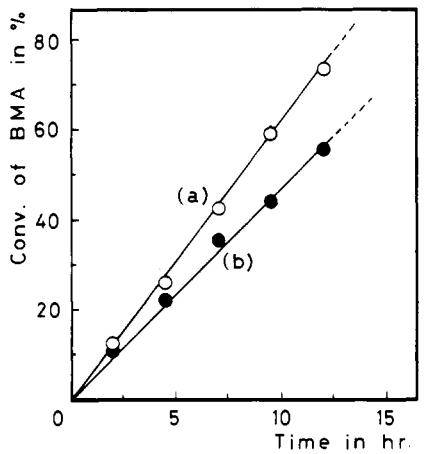


Figure 2. Block copolymerization of butyl methacrylate (BMA) from the living polymer of methyl methacrylate ($\bar{M}n$ = 9100) prepared with (TPP)AlMe (100/100/1), in CH_2Cl_2 15 °C: (a) upon irradiation and (b) in the dark.

It is of particular interest to note that the reaction did not substantially proceed in the dark, as exemplified in the gel permeation chromatogram (GPC) of the reaction mixture (Figure 1). A unimodal, sharp peak of the polymer is observed for the light-induced reaction, while the reaction mixture in the dark only shows the peak corresponding to the porphyrin. Figure 1 also demonstrates the very narrow molecular weight distribution of the polymer formed. The ratio of the weight average to number average molecular weights ($\bar{M}w/\bar{M}n$), as estimated from the GPC by using polystyrene as standard, ranged from 1.06 to 1.20. $\bar{M}n$ as determined by vapor pressure osmometry (VPO) was in good agreement with the value calculated on the basis of the ratio of the monomer to (TPP)AlMe and conversion; for example, for the product from methyl methacrylate/(TPP)AlMe = 200:1 at 100% conversion, $\bar{M}n$(VPO) = 19960, $\bar{M}n$(calcd) = 20040. This behavior indicates the "living" character of the present polymerization reaction.[4]

In accordance with this, block copolymer with narrow molecular weight distribution could be prepared with a quantitative efficiency by the addition of butyl methacrylate to the living prepolymer

(1) For example, (a) Handman, J.; Harriman, A.; Porter, G. *Nature (London)* **1984**, *307*, 534. (b) Okura, I.; Takeuchi, M.; Kim-Thuan, N. *Chem. Lett.* **1980**, 765.

(2) (TPP)AlMe was prepared by the equimolar reaction between 5,10,15,20-tetraphenylporphine and trimethylaluminum in benzene or in methylene chloride, see: Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984.

(3) C=O (δ 178–177 ppm), CH_2 (δ 55–53 ppm), OCH_3 (δ 51 ppm), $-CH_2-CMe(CO_2Me)-$ (δ 45–44 ppm), CH_3 (δ 21–16 ppm) in $CDCl_3$.

(4) For the living polymerization of alkyl methacrylate: (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (b) Allen, R. D.; McGrath, J. E. *Am. Chem. Soc., Polymer Preprints* **1984**, *25*(2), 9. (c) Hatada, K.; Ute, K.; Tanaka, K.; Kitayama, T.; Okamoto, Y. *Polym. J.* **1985**, *17*, 977.

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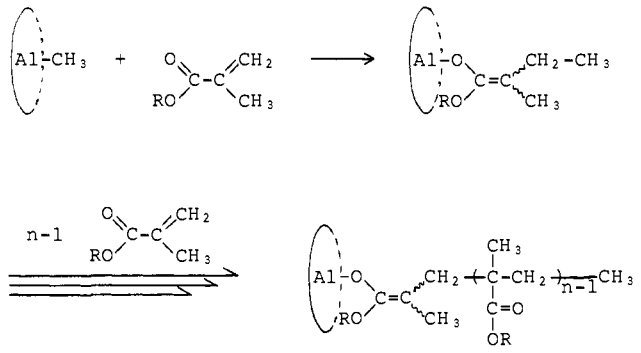
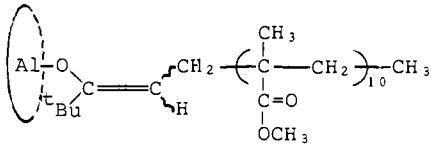
Scheme I



II

of methyl methacrylate. It is particularly noteworthy that moderate but definite acceleration by visible light was observed also in the block copolymerization reaction (Figure 2). In the block copolymerization of butyl methacrylate initiated from the living poly(methyl methacrylate) ($\bar{M}n$ = 9100) prepared with (TPP)AlMe (100/100/1) at 15 °C for 12 h, the conversion was 75% for the light reaction while 54% in the dark reaction; corresponding to this, $\bar{M}n$ = 17 800 ($\bar{M}w/\bar{M}n$ = 1.11) and $\bar{M}n$ = 16 000 ($\bar{M}w/\bar{M}n$ = 1.10), respectively.

In order to obtain further insight into the nature of the reactive species in polymerization, the reaction mixture (living polymer) was subjected to NMR spectral analysis, which can provide very useful information about the group bound to the metal in a porphyrin ring by the virtue of its strong shielding effect. In the reaction of 5 molar equiv of *tert*-butyl methacrylate and (TPP)AlMe in C_6D_6 at 30 °C for 72 h under irradiation, the signal due to Al-CH_3 (δ -5.8 ppm in C_6D_6) disappeared.[5] Among the new signals, a strong singlet at -0.3 ppm (-0.8 ppm in $CDCl_3$) was the most characteristic, the intensity relative to pyrrole-β proton of porphyrin being 8.4:8. In the reaction of the living poly(methyl methacrylate) with 5 molar equiv of *tert*-butyl vinyl ketone, a characteristic signal was observed at -1.5 ppm in $CDCl_3$, which is assigned to *tert*-butyl group of a (porphinato)aluminum enolate I.[6] Therefore, the signal observed at -0.8 ppm in the



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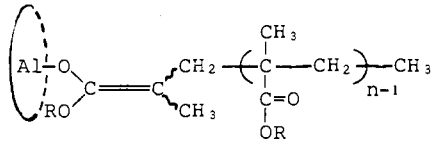

II

former reaction is considered due to an aluminum enolate II, R = *t*-Bu derived from *tert*-butyl methacrylate.[7] These observations indicate that the active species of this polymerization is a (porphinato)aluminum enolate II (see Scheme I). The polymerization probably proceeds via the concerted mechanism, where the approach (coordination) of methacrylate to the aluminum atom and the conjugate addition of methyl or enolate group simultaneously take place.

Thus, not only the addition of (TPP)AlMe to alkyl methacrylate (initiation) but also the addition of (TPP)Al enolate to the methacrylate (every step of propagation) is accelerated by visible light, though to different extents.[8] Aluminum-alkyl or aluminum-enolate bonds cannot be directly excited by visible light but are considered to be activated indirectly by excitation of the porphyrin ring. Thus, the present reaction is a novel type of photocatalysis with metalloporphyrin.

(5) Quantitative incorporation of the methyl group into the terminal of poly(methyl methacrylate) was confirmed by ^{13}C NMR (δ 8.4 ppm in $CDCl_3$).

(6) For (TPP)Al—O—C[C(CH_3)$_3$]=CH—CH_2—Et, formed by the reaction of (TPP)AlEt and *tert*-butyl vinyl ketone, δ -1.46 ppm in $CDCl_3$: Murayama, H.; Inoue, S. *Chem. Lett.* **1985**, 1377.

(7) Other signals at high magnetic field are observed at δ -0.1 to -0.2 ppm and at δ -1.8 to -1.9 ppm (in $CDCl_3$), which are considered due to either =C—CH_2— or =C—CH_3, respectively.

(8) Although there are the examples of photoinduced addition polymerization, light is effective only for the generation of the initiating species. For the example of the initiation with organoaluminum compound: Allen, P. E. M.; Bateup, B. O.; Casey, B. A. *J. Organomet. Chem.* **1971**, *29*, 185.

Hydrolysis of a Distorted Amide Facilitated by Diacids: A Phenomenological Model for the Aspartate Proteinases

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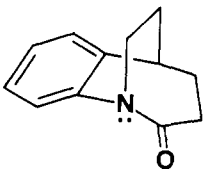
The aspartate proteinases (APases) are hydrolytic enzymes containing two essential aspartate residues.[1] X-ray crystallographic structures of various members have shown close similarity of the active site regions,[2] but the mechanism by which they cleave proteins is said to be[1c] among the most obscure of any protease,[3,4] partly because there exist no satisfactory simple chemical models for precedent.[5] Two possible mechanisms, nucleophilic or general acid/general base, have been proposed.[1-4] Current thinking favors the latter, primarily because experimental detection of covalent intermediates (required in the nucleophilic route) have proven unsuccessful. We have recently presented the synthesis and hydrolysis kinetics of amide I[6a] as well as its x-ray crystal structure



I

and reactivity with β-amino alcohols.[6b] I also shows a striking reactivity toward hydrolysis promoted by certain dicarboxylic acids. Several lines of evidence indicate that the hydrolysis proceeds via the formation of anhydrides as shown in the Scheme I. Firstly, from Table I diacids geometrically capable of forming

(1) (a) *Aspartic Proteinases and Their Inhibitors*; Proceeding of FEBS advanced course no. 84/07; Kosta, V., Ed.; Walter de Gruyer: Berlin, 1985. (b) *Acid Proteases, Structure, Function, and Biology*; Tang, J., Ed.; Plenum Press: New York, 1977; p 95. (c) Fersht, A. *Enzyme Structure and Mechanism*; W. H. Freeman and Co.: New York, 1985: pp 422-426. (d) Fruton, J. P. *Adv. Enzymol.* **1966**, *44*, 1-36.

(2) (a) Hsu, I.-N.; Delbaere, L. T. J.; James, M. N. G.; Hofmann, T. *Nature (London)* **1977**, *266*, 140-145. (b) Subramanian, E.; Swan, I. D. A.; Liu, M.; Davies, D. R.; Jenkins, J. A.; Tickle, I. J.; Blundell, T. L. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 556-559. (c) Jenkins, J. A.; Tickle, I. J.; Sewell, T.; Ungaretti, J.; Wollmer, A.; Blundell, T. In *Acid Proteases, Structure, Function and Biology*; Tang, J., Ed.; Plenum Press: New York, **1977**; pp 43-60. (d) Andreeva, N. S.; Zdanov, A. S.; Gustchina, A. E.; Fedorov, A. A. *J. Biol. Chem.* **1984**, *259*, 11 353-11 365. (e) Bott, R.; Subramanian, E.; Davies, D. R. *Biochemistry* **1982**, *21*, 6956-6962. (f) James, M. N. G.; Sielecki, A. R. *Biochemistry* **1985**, *24*, 3701-3713, and references therein.

(3) For a review of the current status of thinking on the mechanism, see: appendix of Hofmann, T.; Dunn, B. M.; Fink, A. L. in ref 4.

(4) Hofmann, T.; Fink, A. L. *Biochemistry* **1984**, *23*, 5247-5256.

(5) (a) Aldersley, M. F.; Kirby, A. J.; Lancaster, P. W.; McDonald, R. S.; Smith, C. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1487-1495. (b) Kirby, A. J.; McDonald, R. S.; Smith, C. R. *Ibid.* **1974**, 1495-1504. (c) Kluger, R.; Chin, J. *J. Am. Chem. Soc.* **1982**, *104*, 2891-2897.

(6) (a) Somayaji, V.; Brown, R. S. *J. Org. Chem.* **1986**, *51*, 2676-2686. (b) Skorey, K. I.; Somayaji, V.; Brown, R. S.; Ball, R. G. *J. Org. Chem.* **1986**, *51*, 4866-4872.

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