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Diradical polymerization of styrene initiated by ethyl 1-cyano-2-(*p*-methoxyphenyl)cyclopropanecarboxylate with $ZnCl_2$

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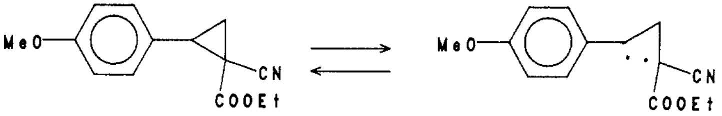
SUMMARY

Ethyl 1-cyano-2-(p-methoxyphenyl)cyclopropanecarboxylate (ECMC) with $ZnCl_2$ initiates the free radical polymerization of styrene (St) at 80°C faster than without $ZnCl_2$. A cycloadduct of St and ECMC is detected. The polymer shows a bimodal molecular weight distribution, and a molecular weight increase is observed with conversion. Based on these results, a diradical initiation and propagation mechanism is proposed.

INTRODUCTION

In a previous paper (1) the polymerization of acrylonitrile initiated by ethyl 1-cyano-2-(p-methoxyphenyl)cyclopropanecarboxylate (ECMC) was described. The electron-donating and electron-accepting substituents on the cyclopropane ring facilitate bond cleavage to polar diradicals which can act as initiators.



In this paper we show that a Lewis acid can accelerate such diradical initiations. ECMC has a cyano group which can complex with $ZnCl_2$ to become a stronger electron-accepting group. We postulated that such complexation would help the bond cleavage of ECMC and thus enhance its initiation efficiency.

Acrylonitrile can complex competitively with $ZnCl_2$ (2-4) and is unsuitable as a monomer in this study. Styrene was therefore chosen as the monomer. The reaction temperature is low enough for the spontaneous thermal polymerization of styrene to be negligible.

RESULTS AND DISCUSSION

Formation of Complex of ECMC with $ZnCl_2$

ECMC forms a complex with $ZnCl_2$ as can be seen in the IR spectra: ECMC has a cyano absorption peak at 2241 cm^{-1}, and in the complex a new absorption peak appears at 2281 cm^{-1}. The shift of cyano group absorption to higher frequency indicates the formation of a coordinate complex of -CN with $ZnCl_2$ as in the case of acrylonitrile(5).

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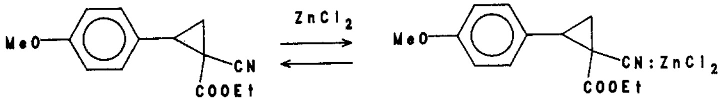


TABLE 1: Time of DPPH Color Fading in Different Conditions[a]

Additive Concentration	Time
$ZnCl_2$ (0.2 M)	35 min.
ECMC (0.1 M)	40 min.
ECMC (0.1 M)/$ZnCl_2$ (0.2 M)	4 min.[b]

[a] Conditions: 100°C in benzene under nitrogen atmosphere in closed vessel. [DPPH] = $2x10^{-3}$M

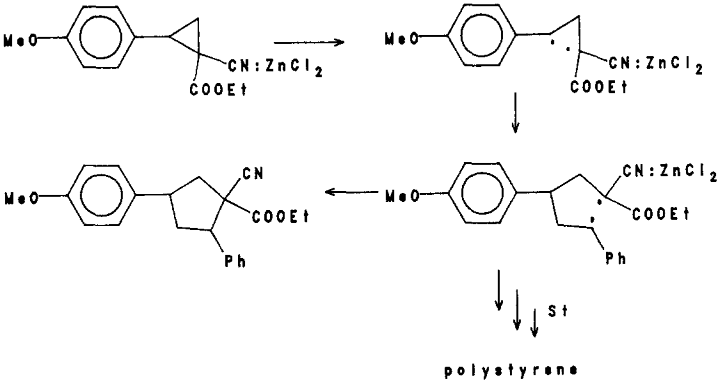
[b] DPPH color disappeared after 10 min. at room temperature.

Free Radical Mechanism

DPPH is a well-known radical scavenger. The rate of radical production in individual systems can be determined from the fading time of it's purple color. Table 1 shows the fading time of DPPH color in different conditions. In the presence of ECMC/$ZnCl_2$ complex, the color disappears very rapidly. This confirms the enhancement effect of $ZnCl_2$ in generating diradicals from ECMC.

Small Molecule Formation

When a St/ECMC/$ZnCl_2$ mixture is heated for several hours, both polymer and low molecular weight products are obtained. After precipitating the polymer in methanol, filtering and evaporating methanol and unreacted St, the residue is analyzed by GC/MS. Besides the St dimers and trimers, small amounts of products with molecular weight 349 are detected, corresponding to a 1:1 ECMC/St adduct. The fragmentation pattern in the mass spectrum agrees with the structure shown below. We propose the following reaction mechanism in analogy to the mechanism proposed for acrylonitrile (1).



Polymerization of Styrene

Table 2 shows the yields of the polymerization of styrene under different conditions. At 80°C and 1.5 hours, both the spontaneous polymerization and ECMC-initiated polymerization are negligible in absence of $ZnCl_2$. The ECMC/$ZnCl_2$ catalyzed polymerization proceeds at a reasonable rate, even though the added $ZnCl_2$ does not completely dissolve in the monomer. As the system is heated for longer time (17 hours), the polymerization of St becomes notable (5.1%). While $ZnCl_2$ or ECMC do not increase the polymer yield much (6.7% and 6.9% respectively), the ECMC/$ZnCl_2$ catalyzed reaction shows substantial acceleration (16.1%). This polymerization is completely inhibited by adding a small amount of TEMPO ($5x10^{-3}$ M). Accordingly a cationic mechanism can be excluded.

TABLE 2: Styrene Bulk Polymerization at 80°C

Initiator	Yield (1.5h)	Yield (17h)
--	0	5.1%
[$ZnCl_2$] = 10.9 mg/ml	0	6.7%
[ECMC] = 0.09 M	0[a]	6.9%
[ECMC] = 0.09 M, [$ZnCl_2$]=10.9 mg/ml	2.1%.[b]	16.1%

[a] After adding CH_3OH the reaction mixture became a little turbid.
[b] $ZnCl_2$ does not completely dissolve in styrene.

SEC analysis shows that the pSt formed spontaneously as well as pSt obtained in the presence of $ZnCl_2$ or ECMC show a single peak at high molecular weight. On the other hand, the pSt obtained from ECMC/$ZnCl_2$ system shows a bimodal molecular weight distribution. The polymer with low molecular weight can be attributed to the cyclization product of diradical propagating chains. After the diradical chains grow long enough, the two reactive ends become independent and the polymer chains propagate in two directions, leading to high molecular weight. Howard (6) and Zimm and Bragg (7) described the "self-termination" of diradical propagating chains to produce low molecular weight products from a theoretical point of view. Our system may provide the first experimental example of a bimodal molecular weight distribution in diradical polymerizations.

Moreover, the propagating diradical chain, after escaping from "self-termination," can undergo intermolecular combination to bring about an additional molecular weight increase. Figure 1 shows the molecular weight increase with conversion for the high MW portion, which is a typical feature of diradical propagation.(8) A control experiment for St polymerization initiated by AIBN shows only one SEC peak and no molecular weight increase with time.

CONCLUSION

Lewis acids are known to accelerate free radical propagation reactions (4). We have shown that a typical Lewis acid, zinc chloride, can also

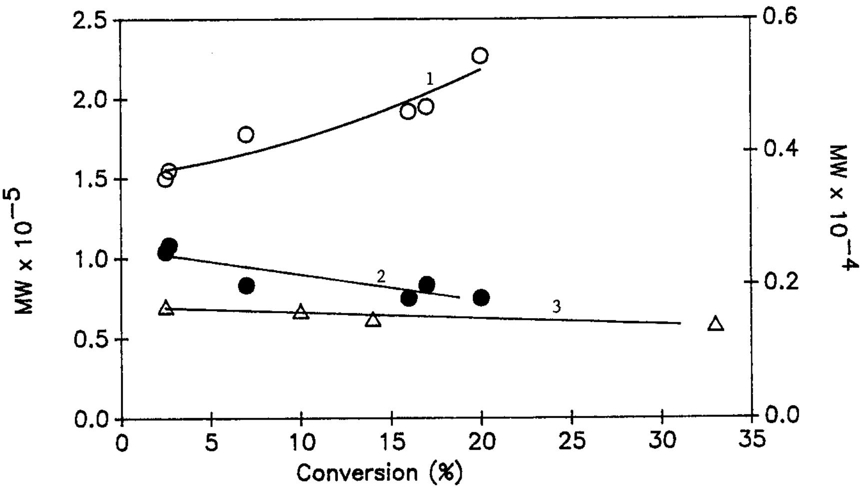


Fig. 1. Relationship between MW and conversion.

1. [ECMC]=$8x10^{-2}$M. [$ZnCl_2$]=10.9 mg/ml, 80°C, high MW portion
2. [ECMC]=$8x10^{-2}$M, [$ZnCl_2$]=10.9 mg/ml, 80°C, low MW portion
3. [AIBN]=$8.5x10^{-3}$M, 60°C.

accelerate the initiation of a free radical polymerization, in this case the cleavage of a donor-acceptor cyclopropane to a trimethylene diradical. We are currently investigating whether such Lewis acids can catalyze formation of tetramethylene diradicals from the respective olefins.

EXPERIMENTAL

Chemicals

Styrene was distilled under reduced pressure twice from calcium hydride before use . ECMC was synthesized as described in a previous paper.(1) $ZnCl_2$ (Mallinckrodt) was dried by melting it at 350°C under argon atmosphere and used immediately. Benzene was purified by distillation from CaH_2.

Instrumentation

Size-exclusion chromatography (SEC) was carried out with combined Shodex A-804 and Phenomemex 104 columns calibrated with polystyrene standards, and with chloroform as eluent and a Spectra-Physics detector at 254 nm. IR spectra were recorded with a Perkin-Elmer 983 spectrophotometer. A chloroform solution of ECMC or the ECMC/$ZnCl_2$ (1:1) mixture was spread on a KBr piece. After the solvent evaporated, a fine film had formed and the IR was recorded. GC/MS were obtained with a Hewlett Packard system: Model 5890 GC, Model 5970 mass Spectrometer and RTE-6 data system.

Polymerization

The polymerizations were run in 15 ml Pyrex tubes with a vacuum-line Teflon valve. Nitrogen was bubbled through the reaction mixture for 3 min. The polymerization tube was then closed off and placed in a temperature-controlled bath and stirred. After a given time, the reactants were poured into excess methanol. The precipitated polymer was filtered off, dried, and weighted.

Small Molecule Products of St/ECMC/$ZnCl_2$ Reaction System

ECMC (78.2 mg), and dry $ZnCl_2$ (43.5 mg) were mixed with 4 ml styrene. Following the procedure described above, the reaction was carried out for 10 hours. The reactants were poured into excess methanol, the polymer was filtered off, and the solvent was evaporated. The residue containing unreacted ECMC and $ZnCl_2$ was dissolved in ether, extracted with water to remove $ZnCl_2$, and then evaporated again. The mixture (214 mg) was analyzed by GC/MS. A 6.0% component in the GC analysis had molecular weight 349 and was assigned to a 1:1 ECMC/St cycloadduct. MS. 349 (100%, M^+), 245 (40%, M^+-$CH_2{=}CHC_6H_5$), 223 (65%, M^+-$CH_3C(CN)COOC_2H_5$), 148 (80%, M^+-$C(CN)COOC_2H_5$ - CHPh)

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REFERENCES

1. Li, T, Willis, T, Padias, AB, Hall, HK Jr *Macromolecules*, (in press).
2. Imoto, M, Otsu, T, Simizu, S (1963) *Makromol. Chem.* **65**: 174
3. Yabumoto, S, Ishii, K, Arita, K *J. Polymer. Sci.* A-I **7**: 1577 (1969)
4. Chen, CSH (1976) *J. Polym. Sci. Polym. Chem. Ed.* **14**: 2109
5. Imoto, M, Otsu, T, Nakabayashi, M. (1963) *Makromol. Chem.* **65**: 194
6. Howard, RR (1950) *Trans. Faraday Soc.* **44**: 204
7. Zimm, BH, Bragg, JK (1952) *J. Polym. Sci.* **9**: 476.
8. Hall, HK, Jr, Padias, AB, Pandya, A, Tanaka, H (1987) *H. Macromolecules* 20: 247.

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