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Synthesis and Polymerization of 4-Methylene-1, 3-Dioxolane Derivatives

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Synopsis : 4-Methylene-1, 3-dioxolane derivatives such as 2-thienyl-4-methylene-1, 3-dioxolane (TMD), 2-thienyl-2-methyl-4-methylene-1, 3-dioxolane (TMMD), and 2-furyl-4-methylene-1, 3-dioxolane (FMD) were synthesized, and their polymerization behaviors were investigated under various conditions. These monomers containing 1, 3-dioxolane moiety were homopolymerized with boron trifluoride as a cationic initiator to give a soluble polymer with low molecular weight. In the presence of radical initiator, although no homopolymerization occurred, it was observed that TMD, TMMD, and FMD were readily copolymerized with a comonomer. The IR and NMR spectra suggest that the homopolymerization proceeds through ring-opening process to give polyketoether structure having thienyl or furyl group.

1. INTRODUCTION

The importance of the radical or cationic ring-opening polymerization among polymerization reactions has recently been recognized. Since Radcliffe[1,2] established that 4-methylene-1, 3-dioxolane derivatives are polymerized via ring-opening, ring-opening polymerization has become a subject of considerable interest to many workers[3,4]. It was reported that 4-methylene-2-phenyl-1, 3-dioxolane[5] and 2, 2-dimethyl-4-methylene-1, 3-dioxolane[6] are homopolymerized by radical or cationic initiator. The cationic polymerization of 2, 2-dimethyl-1, 3-dioxole was also reported by Akkapeddi[7]. Recently, the ring-opening polymerization of 8, 9-benzo-2-methylene-1, 4, 6-trioxaspiro[4, 4]nonane which has a dioxolane moiety has been investigated in our laboratory[8].

In this report we will discuss the polymerization behavior of TMD, TMMD, and FMD which have heterocyclic substituents on dioxolane ring and their copolymerizability with vinyl monomers.

2. EXPERIMENTAL

2-1. Materials and Instruments

Potassium t-butoxide was prepared by the method reported elsewhere[9]. Radical and cationic initiators were purified by a conventional method. Other materials were purified according to the literature methods. Infrared spectra were recorded on a Perkin-Elmer Model 283-B spectrometer. ^{1}H-NMR spectra were obtained with Varian T-60A spectrometer (60MHz).

2-1-1. Preparation of 2-Thienyl-4-Chloromethyl-1, 3-Dioxolane (TCMD)

An ice-cooled mixture of 2-thiophenecarbox-

aldehyde (80g, 0.71mole) and epichlorohydrin (69g, 0.75mole) in 150mL of methylene chloride was slowly added to a cold solution of stannic chloride (10g, 0.038mole) in 30 mL of methylene chloride. The solution was stirred and the addition was continued at such a rate that the temperature did not rise above 25°C for 1h. The resulting orange-brown solution was poured into 150mL of 10% sodium carbonate solution to remove the catalyst. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate overnight. After the solvent was removed under reduced pressure, the residue was fractionally distilled to yield 85g (57%) of TCMD, bp73°C /0.01 torr: ^{1}H-NMR($CDCl_3$) δ 6.8—7.4 (m, protons of thiophene, 3H), 6.1 (d, J=15Hz, methine proton in α-position of thiophene, 1H) 3.6—4.55 (m, —OC$\underline{H}_2$—C$\underline{H}$—, 3H), 3.5 (d of d, J=7Hz, 2Hz, —C$\underline{H}_2$Cl, 2H).

2-1-2. Preparation of 2-Thienyl-4-Methylene-1,3-Dioxolane (TMD)

To a solution of 33g (0.3mole) of Potassium t-butoxide in 300mL of t-butanol, 55g (0.27 mole) of TCMD in 50mL of t-butanol was added dropwise at room temperature. After the mixture was heated under reflux for 12h, the solution was poured into water. The solution was extracted with ethyl ether and the organic layer was dried over anhydrous magnesium sulfate. After the solvent was removed by a rotary evaporator, the residue was fractionally distilled under reduced pressure to yield 43g (95%) of TMD, bp 90°C/4 torr: ^{1}H-NMR ($CDCl_3$) δ 6.6—7.2 (m, protons of thiophene, 3H), 6.15 (s, methine proton in α-position of thiophene, 1H), 3.98—4.6 (m,—OCH_2—, and vinyl 3H), 3.79 (m, vinyl, 1H).

2-1-3. Preparation of 2-Thienyl-2-Methyl-4-Chloromethyl-1,3-Dioxolane (TMCMD)

The reaction of 2-acetylthiophene (31g, 0.25 mole) with epichlorohydrin (23g, 0.25mole) was carried out in the presence of stannic chloride (5g, 0.019mole) with the same manner as described previously. TMCMD was collected at 80°C/10^{-3} torr: yield, 35g (65%); ^{1}H NMR ($CDCl_3$) δ6.6—7.1 (m, protons of thiophene, 3H), 3.65—4.58 (m, OC$\underline{H}_2$—C$\underline{H}$—, 3H), 3.5 (d of d, J=7Hz, 2Hz —C$\underline{H}_2$Cl, 2H), 1.6 (s, —C$\underline{H}_3$, 3H).

2-1-4. Preparation of 2-Thienyl-2-Methyl-4-Methylene-1,3-Dioxolane (TMMD)

TMMD was prepared by dehydrochlorination of TMCMD (30g, 0.14mole) followed by extraction and purification with the same method as TMD. TMMD, bp 63°C/10^{-3} torr was obtained with a high yield (24g, 96%): ^{1}H-NMR ($CDCl_3$) δ6.5—7.0 (m, protons of thiophene, 3H), 4.0 —4.5 (m, —OC$\underline{H}_2$— and vinyl, 3H), 3.65 (m, vinyl, 1H), 1.6 (s, —C$\underline{H}_3$, 3H).

2-1-5. Preparation of 2-Furyl-4-Chloromethyl-1,3-Dioxolane (FCMD)

When 2-furaldehyde (96g, 1mole) was allowed to react with epichlorohydrin(92.5g, 1mole) in the presence of stannic chloride (14g, 0.054 mole) as described above, FCMD, bp 66°C/10^{-3} torr was obtained with a low yield (69g, 36.7 %):^{1}H-NMR ($CDCl_3$) δ7.43(m, proton in 5-position of furan, 1H), 6.27—6.6 (m, protons in 3-, 4-position of furan, 2H), 5.98 (d, J= 15Hz, methine proton in α-position of furan, 1H), 3.68—4.65 (m, —OC$\underline{H}_2$—C$\underline{H}$—, 3H), 3.54 (d of d, J=7 Hz, 2Hz, —C$\underline{H}_2$Cl, 2H)

2-1-6. Preparation of 2-Furyl-4-Methylene-1,3-Dioxolane (FMD)

FCMD (50g, 0.27mole) was treated with potassium t-butoxide (0.28 mole) in t-butanol according to the precedure described above:yield, 38g (93%); bp 70°C/0.1 torr; ^{1}H-NMR ($CDCl_3$) δ7.2 (m, proton in 5-position of furan, 1H), 5.95—6.35 (m, protons in 3-, 4-position of

furan, 2H), 5.9 (s, methine proton in α-position of furan, 1H), 3.95—4.55 (m, $-OCH_2-$ and vinyl, 3H), 3.7 (m, vinyl, 1H).

2-2. Homopolymerization

Polymerization was carried out in sealed tube. After polymerization was completed, the reaction mixture was poured into the mixed solution of 1 : 1 of ether and petroleum ether to precipitate polymer. The polymer was then dried under reduced pressure for a day.

2-3. Copolymerization

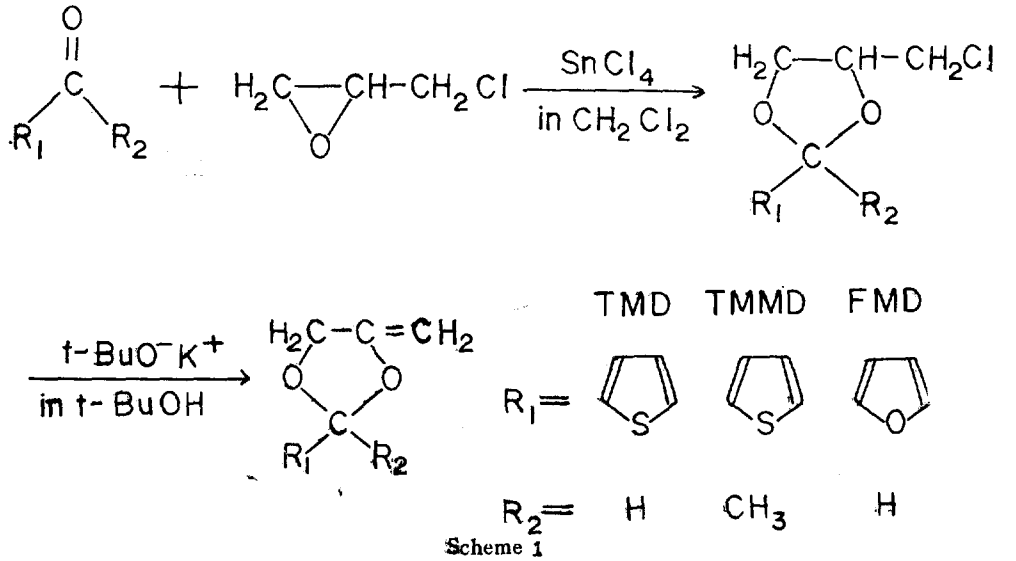
Copolymerization was conducted in sealed tube, and then the copolymer was isolated by pouring the reaction mixture into n-hexane. The copolymer was identified from the IR absorption bands of the functional groups of both monomers.

3. RESULTS AND DISCUSSION

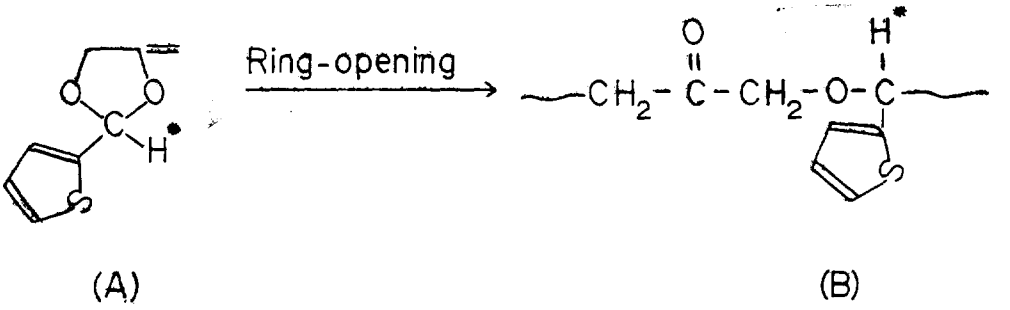
3-1. Preparation of 4-Methylene-1, 3-Dioxolane Derivatives

The synthesis of 4-methylene-1, 3-dioxolane derivatives was conducted by the following reaction reaction scheme 1;

TMD and FMD showed high reactivities toward moisture. When exposed to air, they were slowly polymerized. In order to prevent these undesired reactions, a small amount of base was added during purification and storage. On the other hand, TMMD was quite sta



Scheme 1



Scheme 2

ble in air.

3-2. Homopolymerization

No polymer was obtained when polymerization of TMD, TMMD, or FMD was carried out with DTBT, BPO, or AIBN as a radical initator at various temperature. The reason why no radical homopolymerization occurs is not clear. One possible reason is that the growing species such as the thienyl and the furyl radical due to ring-opening process are not reactive to polymerize.

These monomers, however, were readily polymerized in the presence of cationic intiator such as boron trifluoride etherate at dry ice-aceton temperature. The results of cationic polymerization are summarized in Table 1. The molecular weights of all the homopolymers obtained by cationic initiator were low. The reason is that in the cationic polymerization the chain transfer from monomer and solvent to growing cationic species is more rapid than the rate of propagation.

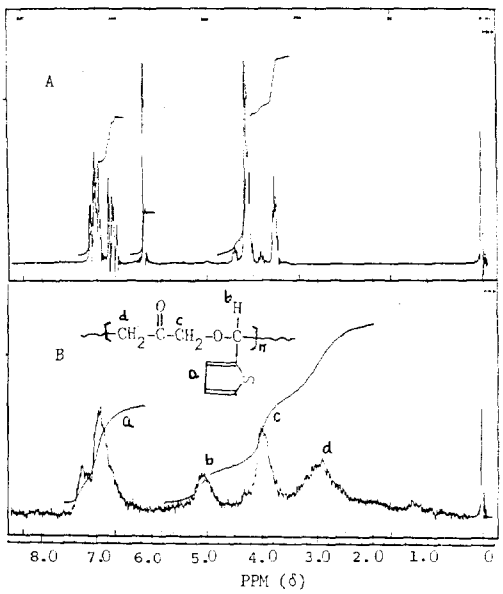


Fig. 1. ^{1}H-NMR spectrum of (A) TMD and (B) homopolymer initiated by BF_3Et_2O.

It was observed that the molecular weight

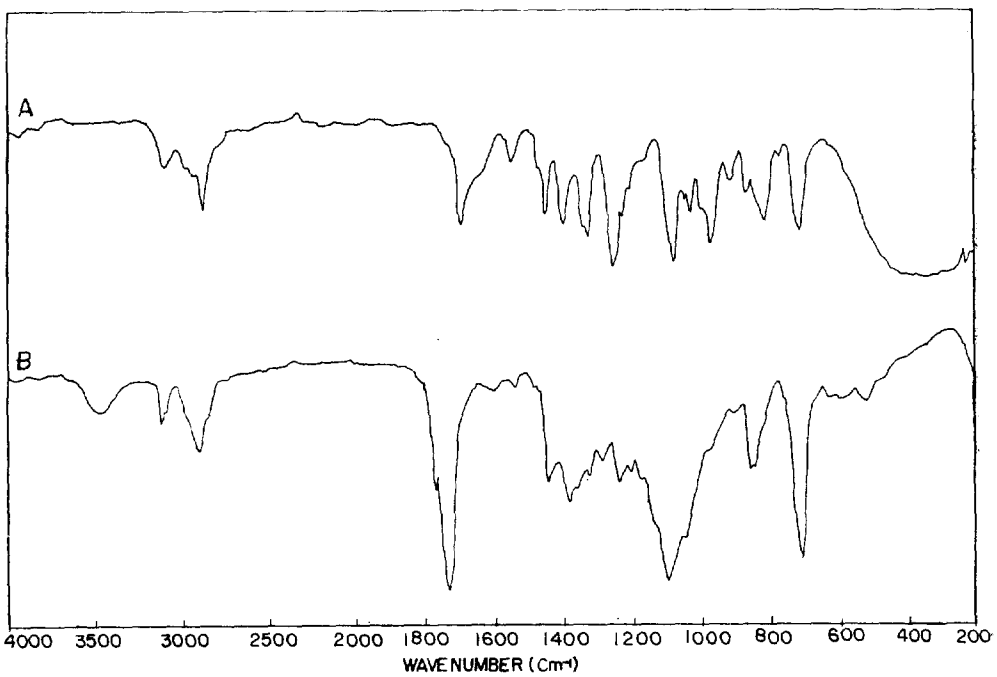


Fig. 2. IR spectrum of (A) TMD and (B) homopolymer initiated by BF_3Et_2O.

and the yield of polymer from TMMD were lower than those of TMD. This may be attributed to the steric hinderance of TMMD. In the case of FMD, an insoluble polymer was yielded, which may be explained by the result of chain-branching reaction to 5-position of furan moiety[10].

The NMR and IR spectra of the polymer obtained from TMD were shown in Figure 1B and Figure 2B. The characteristic carbonyl band due to the ring-opening process appears at 1720 cm^{-1}. The chemical shift of methine proton resulting from the ring-opening process of 1, 3-dioxolane in polymerization shows at 5.05 ppm(B), which is shifted toward upfield compared with the peak at 6.15 ppm(A) of TMD(scheme 2).

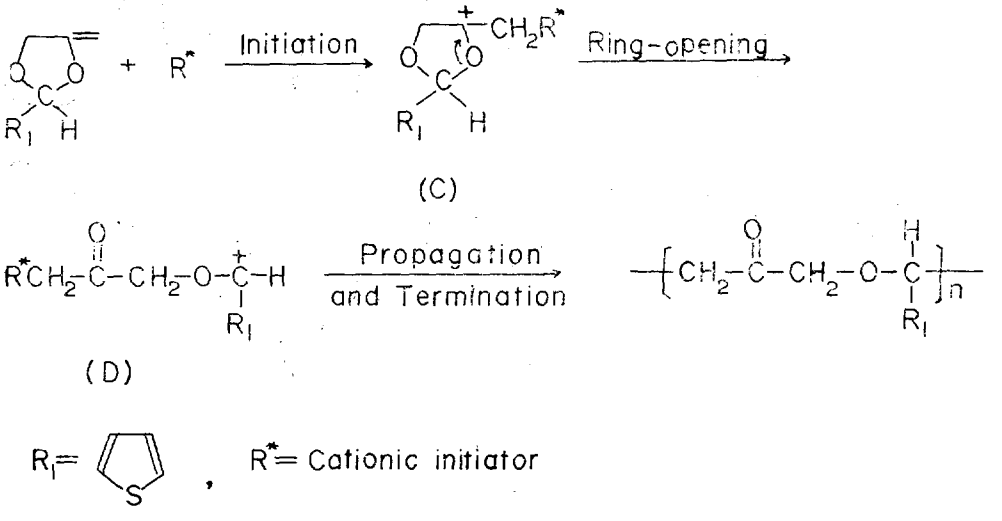
Therefore, it can be considered that catoniic polymerization is proceeded through the ring-opening process involving the conversion of the cyclic carbonium species (C) to an acyclic carbonium one(D) (scheme 3).

Styrene, methyl methacrylate (MMA), and acrylonitrile (AN) were chosen as comonomers for copolymerization study. In contrast with homopolymerization, it can be noted that the copolymerization of TMD, TMMD, or FMD with comonomers was readily carried out by a radical initiator (Table 2). In the case of styrene as a comonomer, homopolystyrene only was obtained by DTBP. This is due to the radical reactivity difference between benzyl ra-

Table 1. Cationic Homopolymerization of TMD, TMMD, and FMD[a]

Exp. No.	Monomer	$\frac{\text{Monomer}}{CH_2Cl_2}$ (g/mL)	Time (hr)	Temp (°C)	η^b_{inh}	Yield	Extent of Ring-Opening (%)
1	TMD	0.3	24	−78	0.05	62	100
2	TMD	0.3	24	−10	0.02	58	100
3	TMMD	0.3	24	−78	0.03	23	100
4[c]	FMD	0.3	24	−78	—	—	—

[a]Boron trifluoride etherate(4mole %) was used as an initiator.
[b]Measured at the concentration of 0.5g/dL in chloroform at 25°C.
[c]This polymer was insoluble in most organic solvent.



Scheme 3

Table 2. Copolymerization of TMD, TMMD, and FMD with Various Comonomers[a]

Exp. No.	Monomer	Comonomer	Monomer/Comonomer (by mole)	Solvent	Initiator	Temp (°C)	Yield (%)	η^{b}_{inh}	Composition[c] of Comonomer in Copolymer (%)
1[d]	TMD	Styrene	1	bulk	DTBP	125	—	—	—
2[d]	TMMD	Styrene	1	〃	〃	〃	—	—	—
3	TMD	MMA	1	〃	〃	〃	51	0.25	90
4	TMD	MMA	3	〃	〃	〃	48	0.42	76
5	FMD	MMA	1	〃	〃	〃	32	0.18	90
6	FMD	MMA	1	〃	AIBN	60	32	0.13	95
7[e]	TMD	AN	1	Toluene	AIBN	60	45[f]	0.05	55
8[e]	FMD	AN	1	Toluene	AIBN	60	53[f]	0.06	56

[a]Total monomer concentration was fixed at 5 mmole; initiator concentration was 3 mole%
[b]Measured at the concentration of 0.5g/dL in chloroform at 25°C.
[c]Calculated from the characteristic peaks in NMR spectrum and elemental analysis.
[d]No copolymer was formed.
[e]monomer/toluene=0.4(g/mL)
[f]Calculated from the soluble portion in toluene.

dical of styrene and thienyl radical resulting from the ring-opening process of TMD. It was identified from NMR and elemental analysis that copolymerization with MMA gave copolymers which were mostly composed of MMA. In the NMR spectrum of TMD-MMA copolymer, especially, the methine proton resonance in the dioxolane ring(A) shown earlier appears at 6.1 ppm (Figure 3A). The characteristic carbonyl band at 1720cm^{-1} due to the ring-opening process was not observed in IR spectrum. These results indicate that small amount of TMD was incorporated into the copolymer without ring-opening(scheme 4).

TMD and FMD were also easily copolymerized with such an electron deficient monomer as AN in the presence of AIBN to give alternating copolymers. The microstructure of the resulting copolymers was identified by NMR, IR, and elemental analysis. The methine proton resonance in dioxolane ring appeared at 6.1 ppm in NMR spectrum (Figure 3B). There was also no detectable carbonyl absorption band due to ring-opening process (Figure 4). The above results support that TMD-AN and

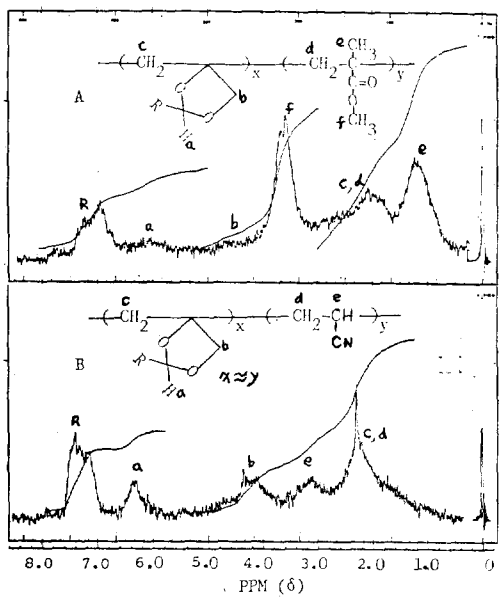
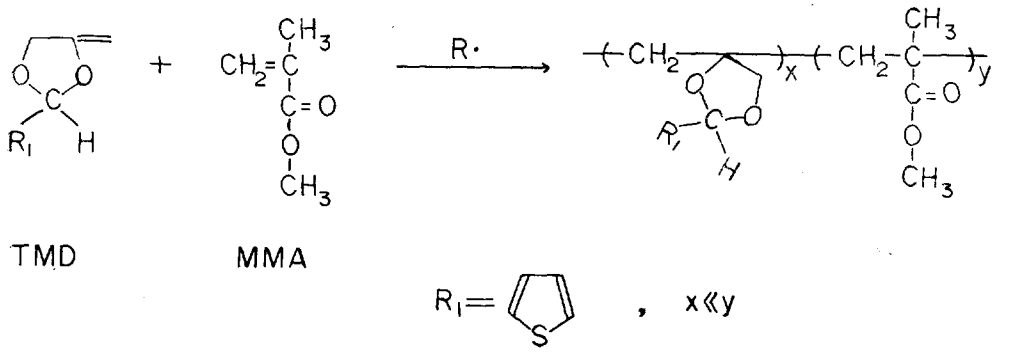


Fig. 3. ^{1}H-NMR spectrum of (A) copolymer of TMD with MMA initiated by DTBP, feed ratio; TMD/MMA=3/1 and (B) copolymer of TMD with AN initiated by AIBN.

FMD-AN copolymers have alternating copolymer structure.

we reported that the copolymerization of new monomer containing 1,3-dioxolane ring



Scheme 4

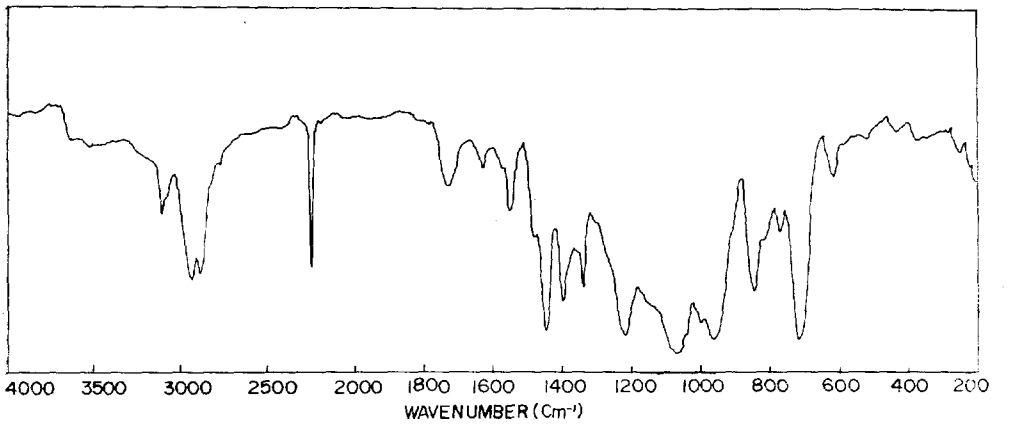


Fig. 4. IR spectrum of copolymer of TMD with AN initiated by AIBN.

moiety with an electron deficient monomer like AN yielded the resulting alternating copolymer[8].

More detailed investigations of the alternating copolymerization of TMD with AN or maleic anhydride as an electron deficient monomer are now in progress and the results will be published in the near future.

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