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Assignment of ^{13}C NMR chemical shift and microstructure of copolymers of 2-chloroethyl vinyl ether-maleic anhydride and *n*-butyl vinyl ether-maleic anhydride

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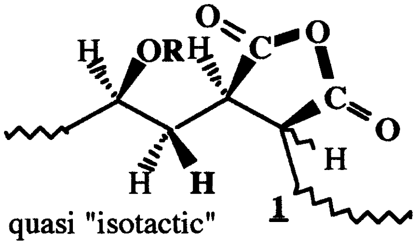
Summary

The chemical shift in the ^{13}C NMR spectra of copolymers of 2-chloroethyl vinyl ether (CEVE) and maleic anhydride (MA), and of n-butyl vinyl ether (BVE) and MA is assigned. It is found that both copolymers are made of completely alternating monomer unit sequences and that the proportion of *cis* linkage configuration at the cyclic MA units is 45 % and 47 % in the CEVE-MA copolymer and in the BVE-MA copolymer, respectively. Depending on the relative orientation of the cyclic anhydride group, quasi "isotactic" and quasi "syndiotactic" tacticity are considered, with quasi "syndiotactic" diads shielding the vinyl ether carbons more effectively.

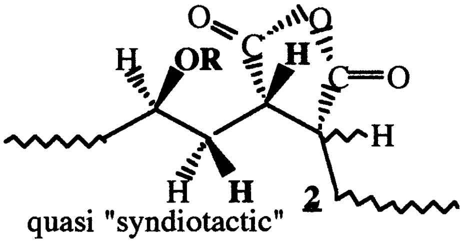
Introduction

Vinyl ethers and maleic anhydride(MA) are known to form copolymers of 1:1 overall composition with radical initiators [1-4]. We have reported that, on the basis of NMR microstructure determination, copolymers of maleic anhydride and isobutyl vinyl ether are made of completely alternating monomer unit sequences with 48 % of the cyclic MA units linked in the *cis* configuration to the backbone of the copolymers [5]. In this article we would like to report chemical shift in the ^{13}C NMR spectra, and the microstructure of copolymers of 2-chloroethyl vinyl ether and MA and of n-butyl vinyl ether and MA.

For a completely alternating copolymer of a vinyl ether and MA, a quasi "isotactic" **1** and a quasi "sydiotactic" **2** diad "tacticity" may be considered by recognising the relative orientation of the cyclic ring of a MA unit with respect to the orientation of the ether side group of the adjacent vinyl ether unit along the backbone of the copolymer.



quasi "isotactic" **1**



quasi "syndiotactic" **2**

Because of the different extent of accessibility of the cyclic anhydride group to the vinyl ether unit depending on the "tacticity", these diad arrangements are expected to influence the chemical shift of vinyl ether carbons differently.

Experimental

Copolymers of maleic anhydride (MA) and 2-chloroethyl vinyl ether (CEVE) were prepared in methyl ethyl ketone at 50.0 °C with the total monomer concentration of

4.00 M and a feed composition of [MA]/[CEVE] = 1.00. Copolymers of n-butyl vinyl ether (BVE) and MA were prepared in chloroform at 50.0 °C with the total monomer concentration of 2.25 M and the feed composition of [MA]/[BVE] = 0.667. Polymerisation was carried out in glass ampoules with 1.0 % 2,2'-azobisisobutyronitrile as the initiator. The glass ampoules were vacuum sealed after two times of freeze-thaw degassing. Copolymers were separated and purified by precipitating in large amounts of boiling (80 - 110 °C) petroleum spirit from the acetone solutions. The ^{13}C NMR spectra were obtained by a Bruker AC-300 NMR spectrometer from the acetone-d_6 solutions of 0.16 - 0.09 g-copolymer/g-acetone concentration in precision NMR tubes; 75.46 MHz with a broad band ^{1}H dual 5 mm probe, over 15 - 20 hour periods at 35.0 °C. The ^{1}H decoupler time and ^{13}C $\pi/2$ pulse time were set at 9.9 and 4.2 µs, respectively. The recycle delay (T_1) was set to 4 s, 2 s and 5 s for the ^{13}C acquisition, distortionless enhancement by polarisation transfer (DEPT) [6] ^{13}C acquisition, and quaternary ^{13}C acquisition, respectively. The J modulation time (Δ) was set to 0.00350 s, which was equivalent to J = 143 Hz ($\Delta = 0.5/J$ for the optimum polarisation and/or sensitivity) for the DEPT experiment. The value of Δ was set to 0.00345 s (J = 145 Hz) for the quaternary ^{13}C experiment. The FID acquired spectra were exponentially Fourier transformed. The DEPT sub-spectra were generated by linear combinations.

Results and Discussion

Fig. 1(a) shows a ^{13}C NMR spectrum of a copolymer of CEVE and MA. The chemical shift of the carbons are assigned according to the quaternary ^{13}C spectrum Fig. 1(b), and the DEPT sub-spectra of methine carbons Fig. 1(c) and methylene carbons Fig. 1(d). The ^{13}C spectrum of a copolymer of BVE and MA is shown in Fig.2. The carbons in the copolymers are numbered as shown in Fig. 1 and Fig. 2.

The methylene carbon of polymer backbone C1 responds to the monomer unit triad sequences in related copolymers [7, 8]. It has been reported that methylene carbon of vinyl ether unit C1 resonates at 42 - 39 ppm in the homopolymer of isobutyl vinyl ether (IBVE) [9] and that it resonates at 37 - 32 ppm in the alternating triad of MA-IBVE-MA unit sequence in the copolymers of IBVE and MA [5]. As seen in Fig.1 and Fig.2, the backbone methylene carbons C1 in the copolymers of CEVE-MA and BVE-MA resonate only at 37 - 32 ppm, which is for the alternating MA-vinyl ether-MA triad, and there is a complete absence of resonance for the semi-alternating monomer unit triads of "vinyl ether-vinyl ether -MA" units and "MA-vinyl ether-vinyl ether" units, which are expected at 40 - 37 ppm. It is considered, therefore, that both copolymers of CEVE-MA and BVE-MA are made of completely alternating monomer unit sequences, which is consistent with the fact that vinyl ethers and MA are incapable of homopolymerising with a radical initiator.

The backbone methine carbons C3 and C4 of MA unit show *cis* and *trans* linkage configurations at the cyclic MA unit, with the *cis* configuration appearing at lower ppm. The assignment has been reported on the basis of the model compounds [10,11]. According to the peak area of the spectra of C4 methine carbon of MA unit in Fig.1 and Fig.2, the proportion of the *cis* linkage configuration is determined to be 45±4 % and 47±4 % in the copolymers of CEVE-MA and BVE-MA, respectively. A very similar result, ie. 48±4 % *cis* proportion, has been reported for the copolymers of IBVE and MA [5]. The substantially large proportion of the *cis* linkage configuration at MA units can be explained when a participation of the electron donor-acceptor complex formed between the comonomers is considered, the complex being attacked by a growing radical at the hexagonal or at the edge-on position of the complex [7.11].

The backbone methylene carbon of vinyl ether unit C1 shows a multiplet peaks at 37 - 32 ppm. The multiplet peaks, which are at least quartets, appear to be made of two

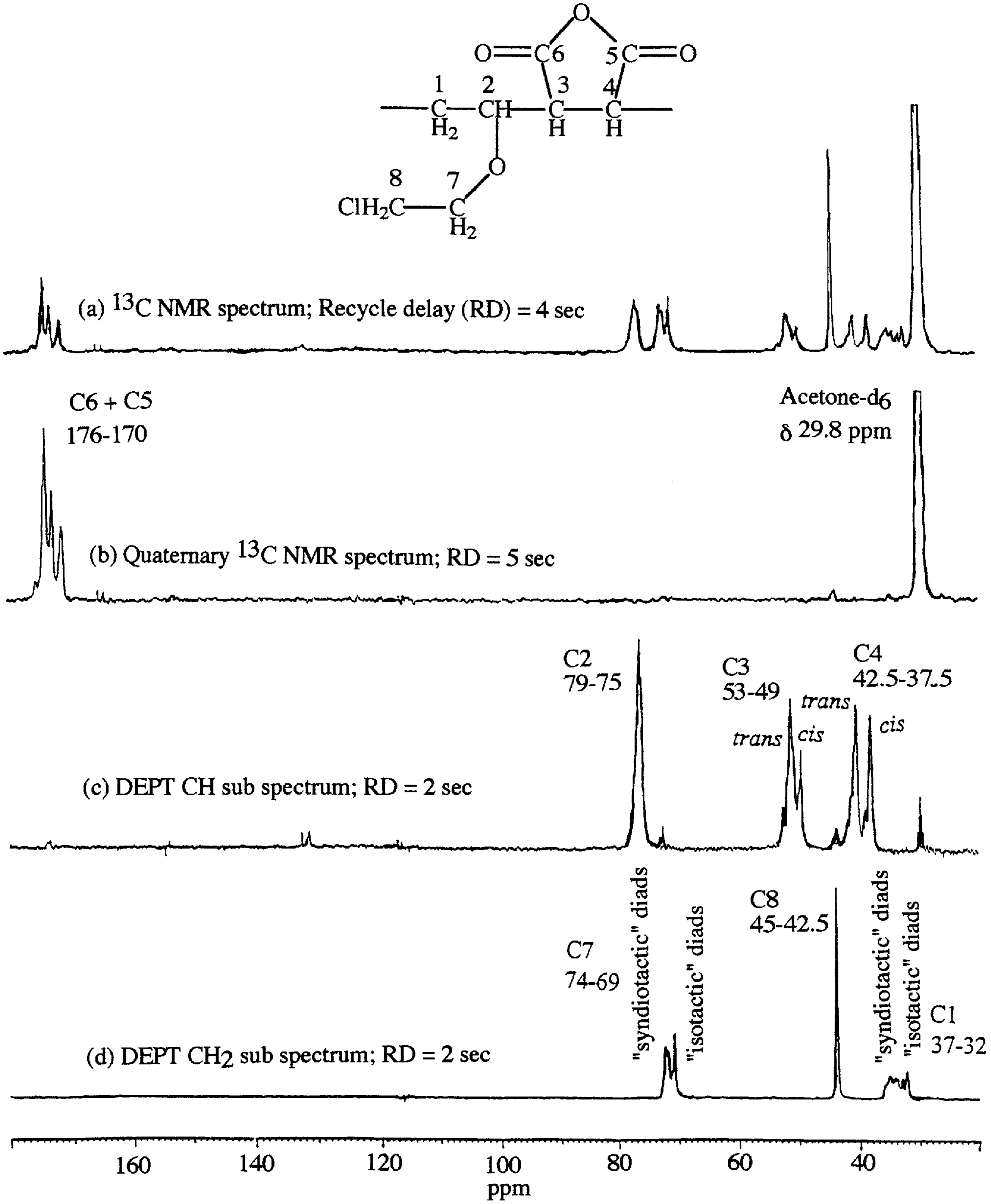


Fig. 1. ^{13}C spectrum of copolymer of chloroethyl vinyl ether and maleic anhydride

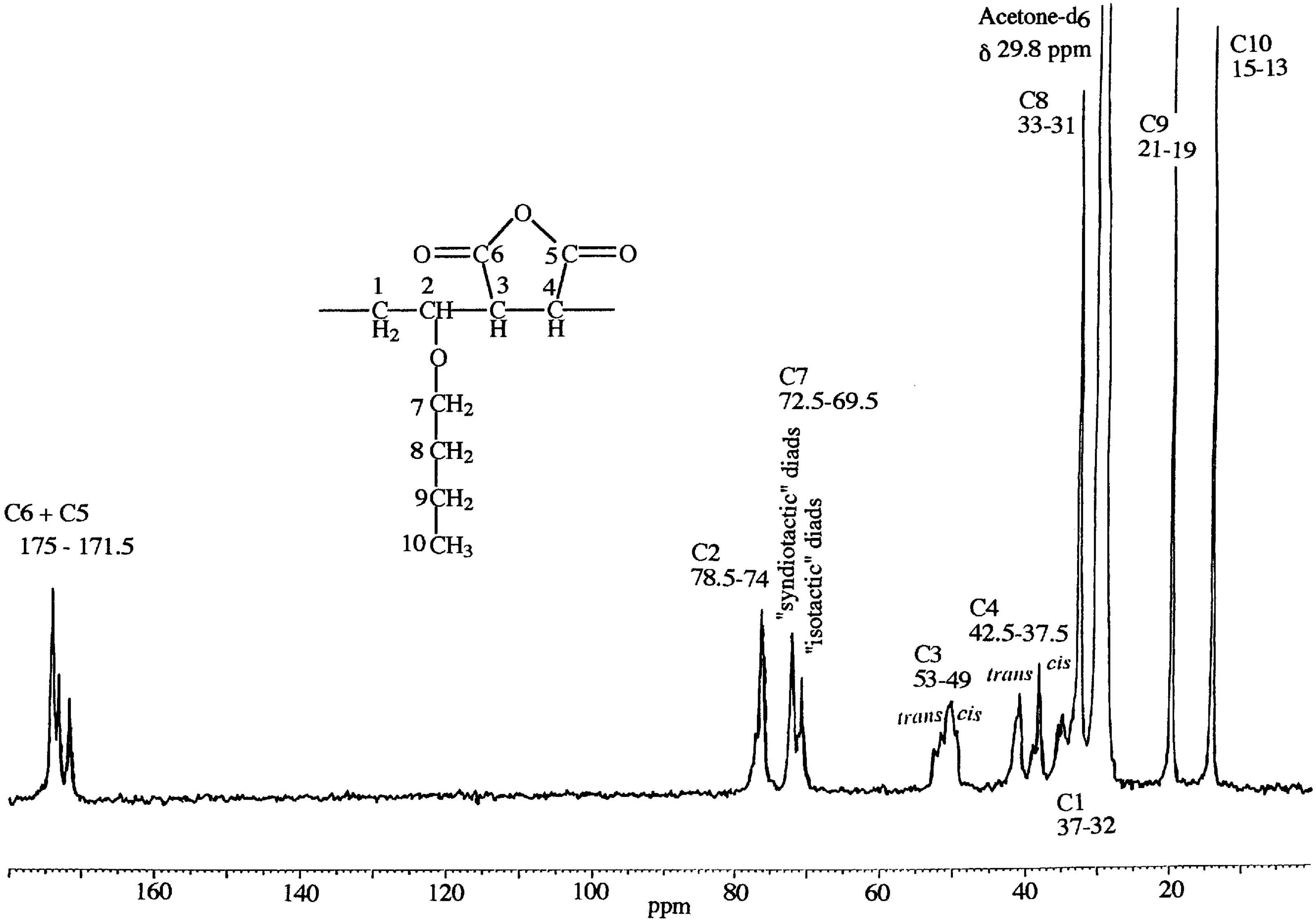


Fig. 2. ^{13}C spectrum of copolymer of n-butyl vinyl ether and maleic anhydride

large groups each of which is made of two or more sub peaks. The side chain methylene carbon C7 of vinyl ether unit also splits in to two groups. It is considered that vinyl ether unit is shielded by the anhydride group of the second adjacent MA unit in the triads differently according to their diad "tacticity". For a completely alternating copolymer of MA and a vinyl ether, the following four overall triad configurations may be possible. These are:

"isotactic-isotactic" triad, and "isotactic-syndiotactic" triad,
"syndiotactic-isotactic" triad and "syndiotactic-syndiotactic" triad,

with each triad having *cis* or *trans* linkage configuration at the second MA unit. The complete set of possible triad configurations are: "iso-*cis*-iso" triad, "iso-*trans*-iso" triad, "iso-*cis*-syndio" triad, "iso-*trans*-syndio" triad, "syndio-*cis*-iso" triad, "syndio-*trans*-iso" triad, "syndio-*cis*-triad" and "syndio-*trans*-syndio" triad. Although in principle all the eight configurations influence neighbouring carbons in NMR differently, it is apparent by the molecular model that "isotactic" diads present much severer steric hindrance to the second MA unit in the triads and prevent its access to the vinyl ether group as compared to the "syndiotactic" diads, the "syndiotactic" diads allowing a better shielding of the vinyl ether group by the second MA unit. The apparent two groups of the sub-peaks of backbone C1 carbon and of the side chain methylene carbon C7 of vinyl ether unit are assigned, from higher ppm to lower ppm, to the "syndiotactic" diads and to the "isotactic" diads.

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