A Bond-forming Initiation Mechanism for Spontaneous Polymerisations Accompanying Diels–Alder Reactions

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A mechanism is proposed for the spontaneous polymerisations which accompany Diels–Alder reactions.

Diels–Alder reactions of electron-rich dienes with electron-poor alkenes are often accompanied by 'adventitious' polymerisations. Beginning with the earliest papers by Diels and Alder,[1] free radical inhibitors have routinely been added to these cycloaddition reactions. In the past, many of these polymerisations could be ascribed to impurities in the reagents or oxygen in the reaction system. However, the improved purity of currently available common vinyl compounds, such as isoprene or acrylonitrile, has meant that they can be stable upon heating even in the absence of a free radical inhibitor

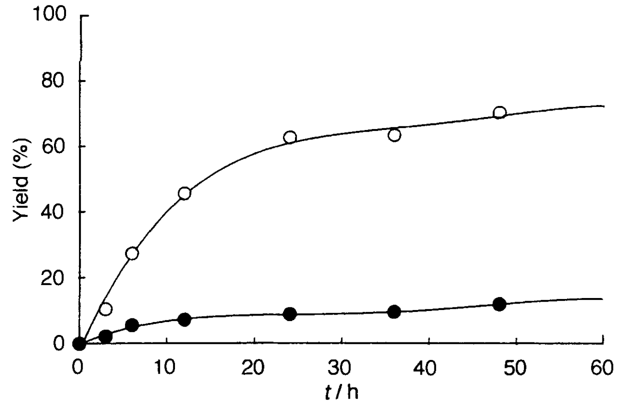
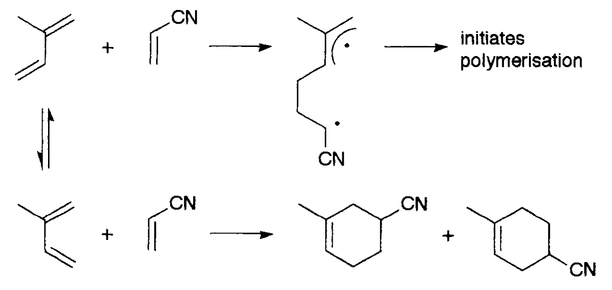


Fig. 1 Time-conversion plots of the spontaneous reaction of isoprene (IP) and acrylonitrile (AN) at 100 °C, [AN] = [IP] = 5.0 mol dm^{-3}: ○ yield cycloadduct, ● yield copolymer

(see below). Nevertheless in reactions of such polymerisable dienes with dienophiles, spontaneous copolymerisations are still observed along with cycloadditions. So the question remains as to which radical species are initiating these polymerisations. We postulate that these polymerisations are initiated by 2-hexene-1,6-diyl diradicals, arising by bond-formation between the s-*trans* diene and the alkene; competitively the planar s-*cis* diene undergoes the classical concerted [4 + 2] cycloaddition. The proposed reaction mechanism is shown in Scheme 1 for the reaction of isoprene and acrylonitrile.

This reaction mechanism extends our bond-forming initiation theory,[2] proposed to explain the spontaneous polymerisations which accompany the [2 + 2] cycloadditions of electron-rich alkenes with electron-poor alkenes. In extensive studies we established that the tetramethylenes, which are the cycloaddition intermediates, are also the true initiators of these polymerizations.[3]

As our first example, in the thermal reaction of isoprene and acrylonitrile in the absence of an inhibitor a significant amount of copolymer accompanies the expected cycloadduct. At 100 °C in bulk after 72 h, 82% of cycloadduct is obtained along with 14% copolymer. Further data are listed in Table 1. We stress that heating either monomer alone under these conditions gives neither cycloaddition nor polymerisation products; they are perfectly stable. Fig. 1 shows typical time-conversion curves, in which each data point represents a separate experiment, showing the reproducibility of our data. The cycloadduct is composed of the two known regioisomers: 1-methyl-4-cyanocyclohex-1-ene (*para* isomer) and 1-methyl-5-cyanocyclohex-1-ene (*meta* isomer) in a ratio of 68:32 as determined by gas chromatography. The fragmentation pattern in the mass spectrum is the same for both isomers,[†] but the identification of these two isomers by derivatisation to the corresponding phthalic acids has been described in the literature.[4] The copolymer composition is the same as that formed by deliberately initiated free radical copolymerisations, namely 56.5% of isoprene for 1:1 feed ratio as determined by elemental analysis. Structures arising from both 1,4- and 3,4-addition of the isoprene unit are present as shown by the NMR spectra. The molecular weight of these polymers is high as shown by inherent viscosities in chloroform solution, which are about 3.0 dl g^{-1} for polymers obtained at 100 °C at 5 mol dm^{-3} for both isoprene and acrylonitrile in 1,2-dichloroethane at different reaction times.



Scheme 1

The thermal reactions of other alkyl-1,3-butadienes with acrylonitrile in absence of inhibitors were also investigated. The results are summarized in Table 1. Cycloaddition competes with copolymerization in the reactions of *trans*-piperylene (*E*-1-methylbuta-1,3-diene) and of 2,3-dimethylbuta-1,3-diene with acrylonitrile. The latter is more reactive overall than the other dienes and also leads to relatively more copolymer. The [4 + 2] cycloadduct of the *trans*-piperylene–acrylonitrile reaction is a mixture of two regioisomers as shown by gas chromatography. The mass spectra of the isomers are identical.[‡] The NMR spectrum of the mixture is not very clear at 250 MHz, but at 500 MHz four doublets of doublets can be observed for the methyl substituent, indicating the presence of the four expected stereoisomers in a 56:33:8:3 ratio. The copolymer obtained in the *trans*-piperylene–acrylonitrile reaction contains equimolar amounts of both reactants. The expected alternating nature of this polymer cannot be confirmed due to the extremely broad peaks in the NMR spectrum. The product of the 2,3-dimethylbuta-1,3-diene–acrylonitrile reaction is the expected [4 + 2] cycloadduct 1,2-dimethyl-4-cyanocyclohex-1-ene as shown by NMR and mass spectroscopy.[§] The copolymer in this case also contains equimolar amounts of both monomers as shown by elemental analysis.

Under similar conditions, *cis*-piperylene (*Z*-1-methylbuta-1,3-diene) and 2,5-dimethylhexa-2,4-diene with acrylonitrile do not lead to any cycloadduct, only copolymer is formed. These reactions are slower than with isoprene as indicated by the reaction times. Again the copolymer composition is the same as for runs initiated with azoisobutyronitrile (AIBN), namely 50:50 for the *cis*-piperylene–acrylonitrile copolymer, as established by elemental analysis. The peaks in the NMR spectra are very broad and cannot be used for sequence analysis.

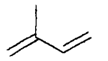
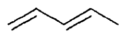
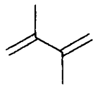
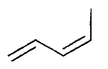
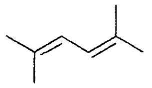
Using cyclic dienes under similar conditions, cyclohexa-1,3-diene with acrylonitrile yields mostly copolymer, while cyclopentadiene reacts even at room temperature, giving exclusively cycloadduct, in agreement with literature data.[5] The high reactivity of cyclopentadiene has been observed in other systems, for example in the cycloaddition with tetracyanoethylene (TCNE)[6] and is ascribed to the fixed planar *cisoid* structure and the short 1,4-distance. The tendency of cyclohexa-1,3-diene to form a copolymer can be ascribed to the non-planarity of this *cis*-diene.

[†] MS (70 eV). *para*-isomer *m/z* (%): 121 (M^+, 30), 106 (M^+ − Me, 19), 94 (M^+ − HCN, 10), 79 (M^+ − $MeCHCH_2$, 29), 68 (M^+ − CH_2CHCN, 100), 53 (M^+ − $CH_2CHC(Me)CH_2$, 30). *meta*-isomer *m/z* (%): 121 (M^+, 49), 106 (M^+ − Me, 41), 94 (M^+ − HCN, 38), 79 (M^+ − $MeCHCH_2$, 100), 68 (M^+ − CH_2CHCN, 52), 53 (M^+ − $CH_2CHC(Me)CH_3CH_2$, 39). ^{1}H NMR ($CDCl_3$) of the mixture: δ 5.44 (0.33H, br s) 5.34 (0.67H, br s), 2.77 (1H, m), 2.35–2.20 (2H, m), 2.10–1.88 (4H, m), 1.67 (3H, s).

[‡] 3-Methyl-(4/5)-cyanocyclohex-1-ene: MS (70 eV) *m/z* (%) 121 (M^+, 23), 106 (M^+ − CH_3, 18), 94 (M^+ − HCN, 20), 79 (M^+ − Me − HCN, 38), 68 (M^+ − CH_2CHCN, 100), 53 (M^+ − $CH_2CHCHCHMe$, 26). ^{1}H NMR ($CDCl_3$): δ 5.74–5.48 (m, 2H) 2.96–2.93 (m, 1H), 2.50–1.82 (m, 6H) 1.20–1.02 (at 250 MHz: four singlets, at 500 MHz: 1.19 dd, 1.17 dd, 1.03 dd, 1.02 dd).

[§] 1,2-Dimethyl-4-cyanocyclohex-1-ene. ^{1}H NMR ($CDCl_3$): δ 2.75 (1H, m), 2.24 (2H br s), 2.17–1.73 (4H, m), 1.62 (6H, s). MS (70 eV) *m/z* (%): 135 (M^+, 39), 120 (M^+ − Me, 30) 109 (M^+ − CN, 15), 93 (M^+ − CN − Me, 62), 82 (M^+ − CH_2CHCN, 58), 67 (M^+ − CH_2CH_2CN − Me, 100), 53 (M^+ − $CH_2CHMeCHMeCH_2$, 28).

Table 1 Reaction of acrylonitrile with alkylbuta-1,3-dienes[a]

Diene	Conc./ mol dm^{-3}	Time/h	Temp./°C	Cycloadduct yield (%)	Copolymer yield (%)
	5	72	100	82	14
	4	24	80	35	9
	5	168	60	24	11
	5	120	70	37	17
	5	72	70	33	40
	5	120	70	0	19
	bulk	48	85	0	32
	bulk	312	80	0	20
	4	264	100	0	13
	3[b]	96	60	0	12
	bulk	120	50	8	61
	bulk	65	28	93	0

[a] *Reaction conditions*: mole ratio 1 : 1, solvent 1,2-dichloroethane, argon atmosphere. [b] Initiated run: AIBN 0.01 mol dm^{-3}.

Similar reproducible spontaneous competition between cycloadditions and polymerisations have already been briefly mentioned in the literature with other 1,3-dienes at room temperature, where adventitious impurities cannot be responsible. Stepek reported that 1-methoxybutadiene and maleic anhydride in concentrated solution spontaneously copolymerise, whereas in dilute solution the Diels–Alder cycloadduct forms.[7] Similarly, Butler and Chen found competition between cycloaddition and spontaneous copolymerisation in the 1-ethoxybutadiene–acrylonitrile system.[8]

To explain the above data on the competition between cycloaddition and polymerisation, the mechanism shown in Scheme 1 is postulated. The results in particular cases can be interpreted in terms of the proportions of planar s-*cis* and s-*trans* and non-planar s-*cis*, conformers of the dienes and also the steric hindrance provided by substituents at either or both terminals. Cycloaddition is favoured by a high proportion of the planar s-*cis* conformer of the diene and a lack of steric hindrance at both terminals of the diene to facilitate the concerted reaction. Copolymerisation is favoured by high s-*trans* content.

This work extends our concept of bond-forming initiation[2,3] in 'charge-transfer' polymerisations to the spontaneous thermal reactions of common 1,3-dienes with electron-poor vinyl compounds. This proposed mechanism can explain the polymerisations which often accompany Diels–Alder reactions in the absence of inhibitors and which are inherent to the reaction.

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