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Radical Copolymerisation of Vinylidene Chloride and Methacrylonitrile, 1

Sequence Microstructure Measured by 220 MHz ¹H NMR

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SUMMARY:
  The radical copolymerisation of vinylidene chloride and methacrylonitrile in bulk and in cyclohexanone solution was studied. The monomer dyad sequence distributions and some of the tetrad and hexad sequences were obtained from 220 MHz ¹H NMR spectra of the copolymers. From the copolymer compositions and sequence information it could be shown that the copolymerisation kinetics deviate from the simple Mayo-Lewis scheme. Small differences were found between the bulk and solution copolymerisations.

Introduction

It is well established that high resolution NMR spectroscopy of polymers can provide much information about polymer microstructure; for copolymers both tacticity and monomer sequence information can often be obtained. The analysis of monomer sequence distributions is a very useful method of studying the copolymerisation kinetics and it has long been recognised that this provides a more sensitive test of the kinetics than making use of just copolymer compositions.

The radical bulk copolymerisation of vinylidene chloride and methacrylonitrile has previously been examined by Block and Spencer[1]. They obtained copolymer compositions and dyad distributions from 60 MHz ¹H NMR and found that the kinetics did not fit the simple scheme of Mayo and Lewis[2]. No reports have appeared of studies of the solution copolymerisation.

In the Mayo-Lewis scheme the reactivity of the polymerising radical is assumed to be influenced by only the terminal monomer unit. This gives rise to four propagation steps which determine the sequence structure and overall composition. Deviations from this simple model can occur for a number of reasons:

1. The influence of penultimate (and other) monomer units on the radical reactivity[3,4]
2. The participation of monomer charge-transfer complexes[5]
3. Solvent effects[6]
4. Depropagation reactions[7,8]
5. Intramolecular transfer reactions[9]
6. Significant head-to-head or tail-to-tail propagations[10].

These deviations give rise to changes in the expected sequence structure and composition but it is not possible usually to distinguish between many of these different possibilities on the basis of composition data alone.

This paper describes the sequence information obtained from vinylidene chloride/methacrylonitrile copolymers by 220 MHz ¹H NMR, with the aim of using this information to elucidate the copolymerisation kinetics and mechanism in bulk and in solution.

Experimental Part

Monomers and solvent were freed from inhibitor (where necessary), dried and fractionally distilled under nitrogen. AIBN was recrystallised twice from abs. ethanol.

Glass ampoules were charged with AIBN (to give $1 \, g \cdot dm^{-3}$), methacrylonitrile (MAN) and, where required, cyclohexanone. The ampoules were then attached to the vacuum line, degassed, filled with vinylidene chloride (VDC) by distillation, and finally sealed under vacuum. Polymerisations were carried out at 60,0°C to between 2 and 5% conversion. The polymers were precipitated in methanol, washed and then dried under vacuum. Most samples were purified by reprecipitation from acetone. Copolymers were prepared from a range of monomer feeds in bulk and in cyclohexanone solution (volume fraction: 0,5).

Some copolymers were prepared using [α-^{14}C]methacrylonitrile, which was synthesised from [carbonyl-^{14}C]acetone by conversion to 2-hydroxyisobutyronitrile[11] followed by dehydration with P_2O_5. This was diluted with inactive monomer and purified to give a sample of activity $0,21 \, \mu Ci \cdot g^{-1}$ [*]. Samples were assayed[12] by liquid scintillation counting using DMF as solvent and a dioxan scintillator solution. Mole fractions n of MAN were calculated from the activities of the copolymer (Cp) and the homopolymer (Co) in counts $\cdot s^{-1} \cdot mg^{-1}$ using the equation:

$$n_{MAN} = \frac{1,445}{\dfrac{Co}{Cp} + 0,445}$$

The 220 MHz ^{1}H NMR spectra were recorded on a Varian HR-220 instrument[**]. Solutions (weight/volume ratio 1:10) in [D_6]acetone at 40°C or in tetrachloroethane at 120°C were employed, with internal TMS and HMDS, respectively.

Results and Discussion

The NMR spectra

The NMR spectra were recorded using [D_6]acetone solutions for copolymers containing more than 25 mole-% MAN (M), and with tetrachloroethane solutions for those with more than 45 mole-% VDC (V). Pyridine solutions were used by Block and Spencer[1], but these were found to give less well resolved spectra than [D_6]acetone and, in addition, were quite unsatisfactory for copolymers containing high proportions of VDC since these were decomposed by the pyridine.

Fig. 1 shows a spectrum of a copolymer containing 71 mole-% VDC in [D_6]acetone solution. The peak assignments are summarised in Tab. 1. The main features of the spectrum have been interpreted by Block and Spencer[1], but there is considerably more fine structure here than they observed at 60 MHz. The spectrum can be divided initially into 4 main groups of peaks: the CH_3 peak and 3 groups arising from CH_2 resonances which are readily assigned to the 3 dyad sequences VV, MV and MM. The VV dyad is clearly resolved into 3 peaks which are assigned to the tetrad sequences VVVV, MVVV and MVVM. Further splitting in these tetrad peaks, which is not observed at 60 MHz, is assigned to hexad sequences. All of the assignments can be made on the basis that replacement of a VDC unit for a MAN unit gives rise to a downfield shift of the CH_2 resonance; these shifts are approx. 0,7 ppm in the dyads, 0,10 ppm in the tetrads and 0,02–0,03 ppm in the hexads. The assignments

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[*] $1 \, Ci = 3,7 \cdot 10^{10} \, s^{-1}$.

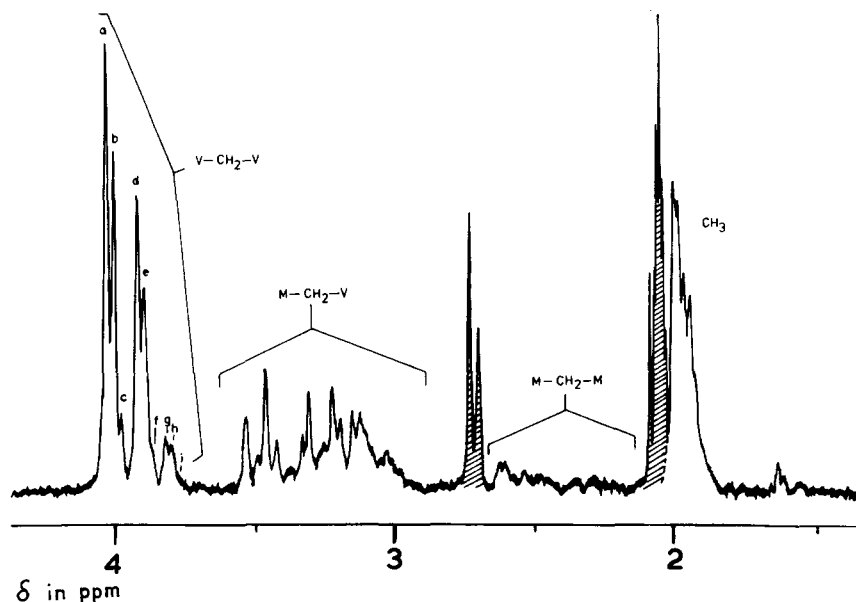[**] The measurements were carried out at the Physico Chemical Measurement Unit at Harwell.

Fig. 1. 220 MHz ^{1}H NMR in [D$_6$]acetone solution of a copolymer containing 71 mole-% VDC. Hatched peaks are acetone ($\delta = 2{,}1$) and traces of impurity ($\delta = 2{,}7$)

Tab. 1. 220 MHz ^{1}H NMR peak assignments

Assignment		Chemical shift	
		in [D$_6$]acetone at 40°C δ (rel. TMS)	in CHCl$_2$—CHCl$_2$ at 120°C δ (rel. HMDS)
CH$_3$		1,8–2,0	1,8–1,95
M—CH$_2$—M		2,1–2,8	2,0–2,7
M—CH$_2$—V		2,8–3,6	2,7–3,4
V—CH$_2$—V		3,7–4,1	3,6–3,9
MV—CH$_2$—VM	MMV—CH$_2$—VMM	3,78 (i)	3,59
	MMV—CH$_2$—VMV	3,80 (h)	3,61
	VMV—CH$_2$—VMV	3,82 (g)	3,63
MV—CH$_2$—VV	MMV—CH$_2$—VVM	3,87 (f)	3,68
	[MMV—CH$_2$—VVV / VMV—CH$_2$—VVM]	3,90 (e)	3,71
	VMV—CH$_2$—VVV	3,93 (d)	3,74
VV—CH$_2$—VV	MVV—CH$_2$—VVM	3,98 (c)	3,77
	MVV—CH$_2$—VVV	4,01 (b)	3,80
	VVV—CH$_2$—VVV	4,04 (a)	3,84

are also consistent with the changes in peak intensities observed with copolymers of different composition. Tetrad and hexad assignments similar to these have been made in the ^{1}H NMR spectra of vinylidene chloride/isobutylene copolymers[13,14]. Further sequence information in the rest of the spectrum is complicated by additional fine structure from tacticity effects arising from the MAN units; in these regions the spectra are too complex and there is insufficient resolution to enable detailed sequence analysis.

Spectra recorded in tetrachloroethane do not show quite as good resolution; the tetrads are resolved but the hexad fine structure is not as well defined. Fig. 2 shows a spectrum
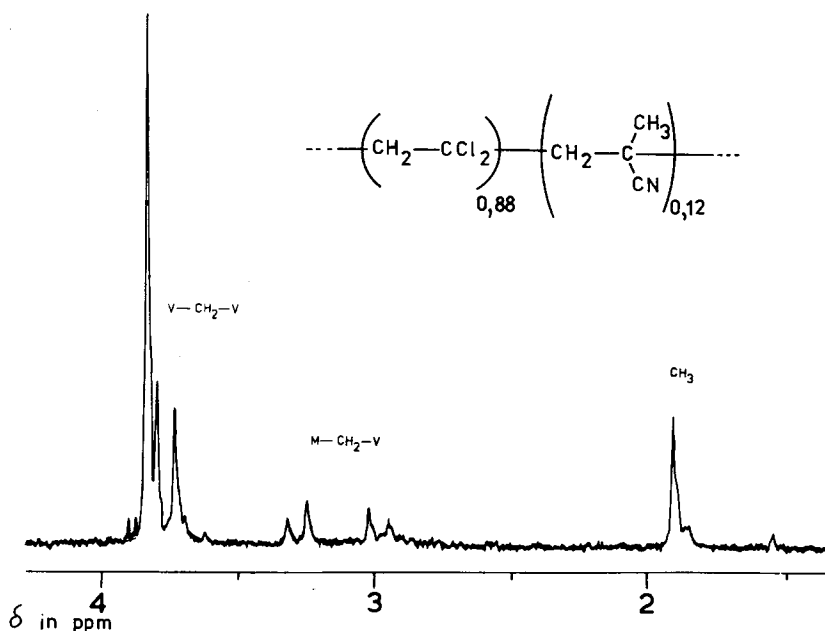

Fig. 2.   220 MHz ^{1}H NMR in tetrachloroethane solution of a copolymer containing 88 mole-% VDC. Hatched peaks ($\delta = 3.9$) are solvent impurities

of a copolymer containing 88 mole-% VDC. This spectrum is quite simple since there is less MAN present to produce complications from tacticity effects. There are negligible MM sequences and most of the VV and MV dyads are now sandwiched between long sequences of VDC units. The MV dyad is now a simple AB quartet pattern arising from the non-equivalence of the two H atoms in the central CH$_2$ group. The CH$_3$ resonance is no longer complicated by tacticity effects and exhibits some splitting indicative of monomer triad sequences. Unfortunately the resolution of the CH$_3$ peak is not as good as observed[15] in vinylidene chloride/methyl methacrylate copolymers where the α-methyl resonance occurs over a wider chemical shift range ($\delta = 0.9$ to 2.0) and triad sequences are resolved.

Tab. 2. Copolymer compositions (in mole-% VDC)

Mole-% VDC in monomer feed	Copolymer composition in mole-% resulting from					
	bulk copolymerisation			solution copolymerisation		
	by NMR in [D$_6$]acetone	by NMR in CHCl$_2$–CHCl$_2$	by ^{14}C labelling	by NMR in [D$_6$]acetone	by NMR in CHCl$_2$–CHCl$_2$	by ^{14}C labelling
10	5±1			4,5±1		
20	9±1		9 ±1	10 ±1		10,5±1
30	14±1			14,5±1		
40	18±1		19 ±1	21 ±2		22 ±1
50	26±2			27 ±2		
60	33±2		35,5±1	36 ±2		39 ±1
70	43±2	46 ±3		48 ±2	49±2	
75	54±2	57 ±2		52 ±2	54±2	
80	57±3	62 ±2		60 ±2	62±2	
85	68±3	69 ±2	70,5±1	70 ±3	71±2	71 ±1
90		79,5±1			79±1	
93					84±1	
94		89 ±1	88,4±0,5		88±1	87,6±0,5
95		90 ±1				
96					92±1	
97		93,5±1	93,3±0,5		94±1	92,8±0,5

Copolymer compositions

Copolymer compositions were calculated from the NMR spectra by measuring the relevant peak areas and applying the following equations.

$$n_{\text{VDC}} = 1 - (2\text{ACH}_3/3\text{ACH}_2) \tag{1}$$

$$n_{\text{VDC}} = \frac{\text{Avv} + \frac{1}{2}\text{Avm}}{\text{Avv} + \text{Avm} + \text{Amm}} \tag{2}$$

where ACH_3 = area of CH_3 peak; ACH_2 = area of all CH_2 peaks; Avv = area of vv peaks; Avm = area of vm peaks; Amm = area of mm peaks.

Averaged values of n_{VDC} were obtained from the two methods of calculation. The calculated compositions are presented in Tab. 2 together with compositions obtained from the labelling experiments which were carried out as an independent check. It can be seen that the NMR and ^{14}C composition results agree well. Close examination shows that there is a small systematic difference between the bulk and solution prepared copolymers.

Tests of the copolymerisation kinetics

Composition data

For copolymerisations which obey the Mayo-Lewis kinetic scheme the instantaneous copolymer composition $(m_1/m_2 = f)$ is related to the monomer feed $([M_1]/[M_2] = F)$ by the equation

$$\frac{m_1}{m_2} = \left(1 + r_1 \frac{[M_1]}{[M_2]}\right)\left(1 + r_2 \frac{[M_2]}{[M_1]}\right)^{-1}$$

where r_1 and r_2 are the usual reactivity ratios. In practice this is applied to low conversion copolymerisations. The method of Kelen and Tüdős[16] was used here for fitting the composition and feed data to this equation. The two functions η and ε are plotted against one another where

$$\eta = \frac{F(1 - 1/f)}{\alpha + F^2/f}, \qquad \varepsilon = \frac{F^2/f}{\alpha + F^2/f}$$

and α is a numerical constant chosen to give a suitable spread of the data. This method is a modification of the Fineman-Ross[17] equation but produces a more convenient plot for which the errors are linear, and hence a least squares analysis can be properly applied if required. A copolymerisation which follows Mayo-Lewis kinetics should produce a good straight line fit to a Kelen-Tüdős plot with intercepts at $\varepsilon = 1$ of r_1, and at $\varepsilon = 0$ of $-r_2/\alpha$. If the kinetics deviate from this scheme a curved plot results.

The plots are shown in Figs. 3 and 4. The bulk copolymerisation can be seen to fit a curve. A least squares straight line fit to this gives reactivity ratios of r_1 (VDC) = 0,42 ± 0,06 (S. D.) and r_2 (MAN) = 2,7 ± 0,3, whereas the two intercepts from the curved fit give significantly different values of 0,50 and 2,1, respectively. Block and Spencer[1] obtained values of approx. 0,37 and 1,7. The solution copolymerisation results show only slight curvature with reactivity ratios of 0,42 ± 0,04 and 2,45 ± 0,2 for a straight line fit and 0,47 and 2,2 from the curved fit. Similar illustrations of the curvature can be obtained by constructing Fineman-Ross plots.
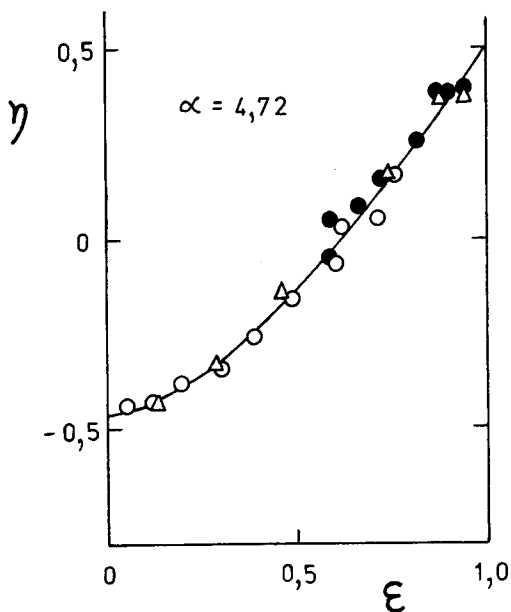
Fig.3. Kelen-Tüdős plot of composition results from copolymerisations in bulk. (o): NMR in $[D_6]$acetone; (●): NMR in $CHCl_2$—$CHCl_2$; (△): ^{14}C labelling
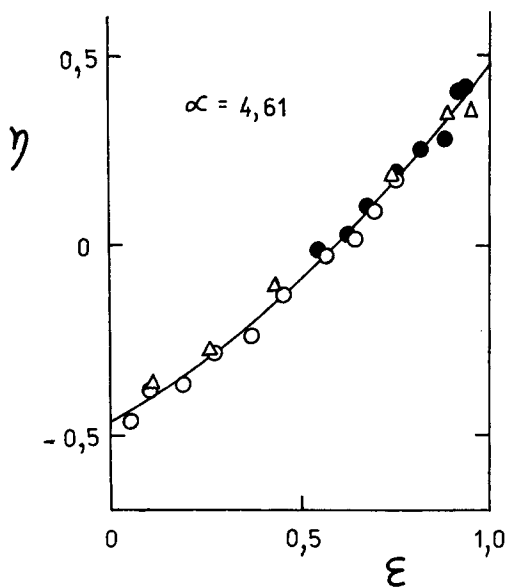

Fig. 4. Kelen-Tüdős plot of composition results from copolymerisations in solution. (o): NMR in $[D_6]$acetone; (●): NMR in $CHCl_2$—$CHCl_2$; (△): ^{14}C labelling

Clearly on the basis of compositions both the bulk and solution copolymerisations appear to deviate to different extents from Mayo-Lewis kinetics.

Dyad sequence distributions

The Mayo-Lewis scheme may also be tested by examining the monomer dyad sequences in the copolymers. A good way of doing this is by the method of Chujo et al.[18] in which the reactivity ratios are calculated for each individual sample from the dyad distributions and the monomer feed. The relevant equations are

$$r_1 = 2 \frac{(11)}{(12)} \frac{[M_2]}{[M_1]} \quad \text{and} \quad r_2 = 2 \frac{(22)}{(12)} \frac{[M_1]}{[M_2]}$$

where (11), (12) and (22) are the fractions of the three types of dyads in the copolymer. If Mayo-Lewis kinetics apply the calculated reactivity ratios should be the same for samples prepared with different monomer feeds.
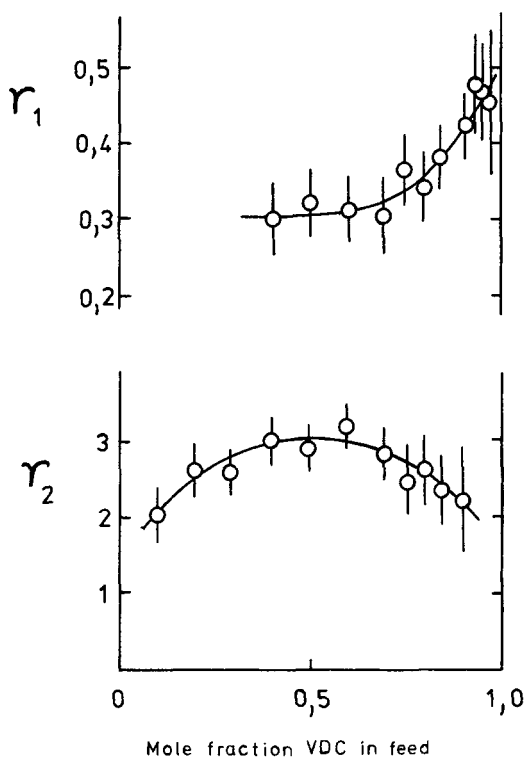

Fig. 5. Reactivity ratios calculated from measured dyad distributions of copolymers prepared in bulk

Mole fraction VDC in feed

The results of these calculations are shown in Figs. 5 and 6. For bulk copolymerisation both r_1 and r_2 vary with monomer feed. For the solution results the variation is not so large although there is a clear increase in r_1 for feeds rich in VDC. These results confirm in more detail the conclusions from the composition data that both systems deviate to different extents from Mayo-Lewis kinetics.
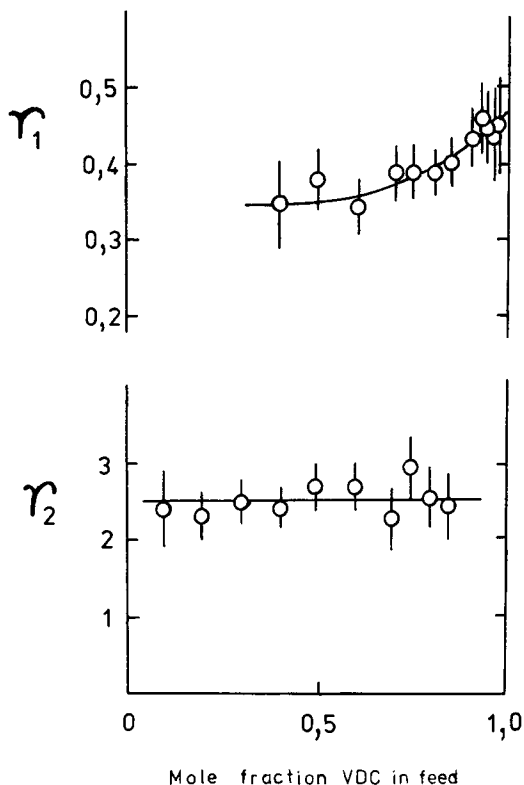
Fig. 6. Reactivity ratios calculated from measured dyad distributions of copolymers prepared in solution

Mole fraction VDC in feed

Tetrad sequence distributions

The measured tetrad sequences VVVV, MVVV and MVVM have been compared with distributions predicted from the Mayo-Lewis scheme. These distributions were calculated using the computer program devised by Harwood[19]. Some results are shown in Figs. 7 and 8. It is interesting that these distributions are almost identical for the bulk and solution copolymerisations and give acceptable fits to reactivity ratios of $r_1 = 0,40$ and $r_2 = 2,5$. These tetrad distributions are more sensitive to values of r_1 than r_2 and therefore little significance should be attached to this value of r_2. For r_1 the value of 0,40 gives noticeably better fits than using 0,35 or 0,45. Unfortunately these tetrad distributions are not as helpful in elucidating the kinetics as might have been expected.

Conclusions

The composition and dyad sequence data have confirmed that bulk copolymerisation of vinylidene chloride and methacrylonitrile deviates from Mayo-Lewis kinetics. The reactivity ratios determined vary with monomer feed within the ranges $r_1 = 0,30$ to 0,48 and $r_2 = 2,0$ to 3,0. The copolymerisation in cyclohexanone solution (volume fraction: 0,5) also shows
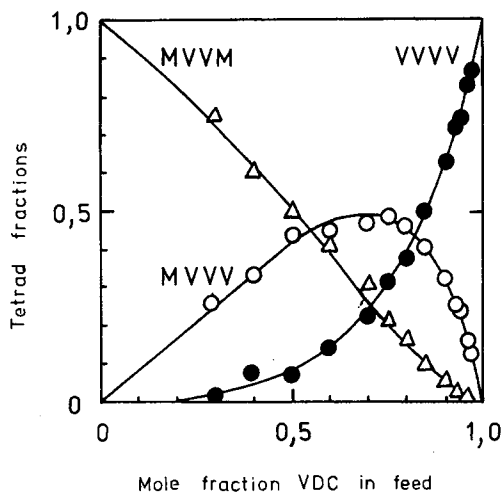
Fig. 7. Measured tetrad distributions VVVV (●), MVVV (○) and MVVM (△) in bulk prepared copolymers compared with distributions calculated from $r_1 = 0,40$ and $r_2 = 2,5$ (solid lines)
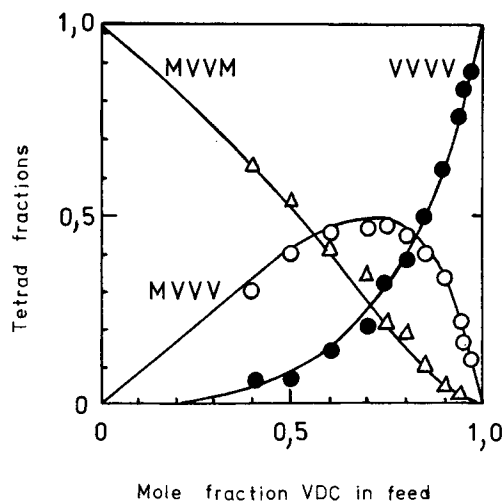

Fig. 8. Measured tetrad distributions VVVV (●), MVVV (○) and MVVM (△) in solution prepared copolymers compared with distributions calculated from $r_1 = 0,40$ and $r_2 = 2,5$ (solid lines)

deviations, but these are less marked than in bulk and there are only small deviations from the reactivity ratios $r_1 = 0,40$ and $r_2 = 2,5$, and therefore shows close to ideal random behaviour for which $r_1 r_2 = 1,0$.

It is perhaps not surprising that the bulk and solution copolymerisations show some differences since the bulk copolymerisation is heterogeneous. This could indicate that solvation effects are important and experiments using different solvents at different concentrations are in progress.

With the available sequence information it is not possible to test directly for penultimate effects since triad distributions are required to do this. However, work with ^{13}C NMR spectroscopy is also in progress and from this it is possible to obtain all of the triad distributions

from the resonances of the quaternary C atoms in the polymer backbone[20]. With this additional information the different kinetic schemes which may be responsible for these deviations will be tested[21].

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