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Copolymerisation of Unsaturated Organophosphorus Monomers

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The present state of the problem of the copolymerisation of unsaturated organophosphorus monomers is considered. Quantitative data on their reactivities in the radical polymerisation processes are surveyed and analysed critically, the place of these monomers among other types of unsaturated compounds is defined, and the organophosphorus monomers most promising from the standpoint of the modification of polymeric materials by copolymerisation methods are specified. The review is based on data published up to the end of 1978.
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I. INTRODUCTION

Heat resistance, to which much attention is devoted nowadays, strong adhesion, and the formation of complexes, ion-exchange, and other properties are responsible for the interest in the practical applications of organophosphorus polymers[1]. The majority of polymers of industrial importance burn in air, which constitutes a serious obstacle to their wider and more comprehensive application. Although the introduction of fire-proofing agents into polymers is not able to prevent completely the decomposition of organic polymers on contact with flames, nevertheless it diminishes significantly the rate of propagation of the flame and can even lead to the formation of a self-extinguishing material. The best effect is achieved when chemically active fire-proofing agents[2], particularly organophosphorus monomers (OPM), are used; here the combustion-retarding agent is introduced into the polymer chain, i.e. is an integral part of the polymer. The simplest and most effective method of constructing such a chain involves the copolymerisation of OPM with other unsaturated monomers. Numerous communications devoted to the copolymerisation of unsaturated OPM including reviews and monographs[3-5], have been published hitherto, but the latest review[5] is already more than 10 years old.

Apart from purely practical applications, the copolymerisation method is of interest because it permits a quantitative estimate of the relative reactivities of monomers and polymeric radicals and makes it possible to obtain valuable information for the determination of the mechanisms of radical reactions. Whereas kinetic studies on the homopolymerisation of OPM are as yet restricted to a narrow range of monomers[6-9], the quantitative data on copolymerisation, from which correct conclusions about the influence of the structure of the OPM on their reactivity can be drawn, are fairly extensive. In the present review an attempt is made to survey and interpret critically data on the copolymerisation of OPM precisely from this point of view.

Mainly radical copolymerisation is considered, since problems of the ionic copolymerisation of the OPM have so far been dealt with only in isolated reports[10-12], where it is concluded that the vinyl derivatives of phosphorus have a very low reactivity in anionic and ionic-coordination copolymerisation. Qualitative information about the copolymerisation of unsaturated OPM is discussed only when necessary. The semivinyl copolymerisation of derivatives of tricoordinate phosphorus has been described in a recent review[13]; The semivinyl polymerisation of OPM with SO_2 is dealt with by Faizullin et al.[14]. The properties and applications of the phosphorus-containing copolymers formed will not be considered in this review, since independent reviews have been devoted to these problems[2,15-18].

The polymerisation and copolymerisation of unsaturated OPM lead to carbochain polymers with the phosphorus in the side chain. Depending on the relative positions of the phosphorus atom and the double bond and also on the reactivity of the monomer, it is useful to divide all OPM into four types (typical examples are indicated below; X = OH, OAlk, OAr, NR_2, Alk, Ar, $CH_2=CH$, etc.).

A. OPM with the phosphorus atom linked directly to a vinyl or substituted vinyl group:

$$CH_2=CHP(O)X_2,\ CH_2=C(R)-P(O)X_2,\ CH_2=CHPX_2\ .$$

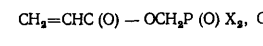
B. OPM with a diene group at the phosphorus atom:

$$CH_2=CH-CH=CHP(O)X_2,\ CH_2=CP(O)X_2-CH=CH_2\ ,$$
$$CH_2=CP(O)X_2-CP(O)X_2=CH_2\ .$$

C. OPM with the phosphorus atom linked by a double bond via oxygen, nitrogen, a methylene group, or their combination:

$$CH_2=CHOP(O)X_2,\ CH_2=CH-CH_2P(O)X_2,\ CH_2=CH-CH_2OP(O)X_2\ .$$

D. OPM with the phosphorus atom remote from the double bond:



Not only the copolymerisation but also the homopolymerisation of OPM proceeds in very different ways depending on the type to which they belong. When the phosphorus atom is fairly remote from the C = C bond (type D), polymers with a high molecular weight are obtained; no significant differences associated with the influence of the phosphorus atom are observed, since we are virtually dealing only with the polymerisation of styrene, acrylate, etc. If the phosphorus atom is attached directly to the double bond or is separated from it by an oxygen atom (types A and C), polymers with a low molecular weight are obtained owing to specific chain transfer processes, for the explanation of which a number of schemes have been proposed[6,19-22]. When the allyl group is

present in the monomer (type C), the characteristics of allyl polymerisation become of primary importance, which also leads to oligomers. The polymerisation of 1,3-diene OPM (type B) yields polymers[23,24] or copolymers[22,25] with a high molecular weight, depending on their structure.

Organophosphorus monomers undergo copolymerisation virtually with all the usual vinyl monomers, but the yields and molecular weights of the copolymers in most cases decrease with increasing content of OPM units in the macrochain[6,22,37,38]. However, when comparatively small amounts of the phosphorus-containing monomer are used, it is possible to achieve high yields of copolymers with a sufficient phosphorus content to impart to them useful properties and to achieve a satisfactory molecular weight. The introduction of small amounts of phosphorus frequently imparts to polymers new valuable qualities without a significant impairment of their physicomechanical properties. The modification of the known polymers by small amounts of phosphorus is therefore at present of greater practical interest than the synthesis of new organophosphorus polymers.

The Alfrey–Price $Q-e$ scheme is most widely used to characterise the behaviour of monomers in radical copolymerisation reactions. In the present review the parameters Q and e for OPM have been recalculated using Greenley's recently published[26] average values of $\bar{Q}-\bar{e}$ for comonomers, which have been determined by the method of least squares taking into account the probable errors in the determination of the copolymerisation constants. In certain cases Greenley's values differ significantly from the "average" values found by Young[27] and usually employed. Furthermore, in many instances we corrected the values of Q and e for the OPM because sometimes[28-30] the authors of the original communications gave preference to chemically less reasonable values of e of the two possible ones in the solution of the quadratic Alfrey–Price equation. For those compounds where this was possible, we also calculated the average parameters Q and e from the Lüssi equation[31] using Greenley's[26] criterion (the subdivision of monomers into groups based on the degree of reliability, the use of at least three–four independent determinations of the constants r_1 and r_2 for copolymerisation with comonomers belonging to a group which is not below Greenley's group III). In addition we believe it is necessary to use data for not less than three comonomers and to exclude from consideration systems with acid components†, since all the OPM discussed in this review form strong hydrogen bonds with them[32]. In the Tables below Greenley's groups are denoted by Roman numerals, n is the number of independent determinations of r_1 and r_2 used for the calculation, and R is the correlation coefficient. We emphasize that in the case of OPM the use of the Lüssi equation is particularly convenient, since this equation does not include the copolymerisation constants r_1 referring to the phosphorus-containing macroradical, which are as a rule determined with a lower relative accuracy than the constants r_2 referring to the comonomer macroradical. Furthermore, systems with r_1, $r_2 > 1$ and $r_1 = 0$ can be used to calculate $\bar{Q}$ and $\bar{e}$ by the Lüssi–Greenley method.

The following abbreviations have been adopted in this review: (1) for the names of organic monomers: AA = acrylic acid, AN = acrylonitrile, VA = vinyl acetate, VDC = vinylidene chloride, VC = vinyl chloride, DMA = dodecyl methacrylate, MA = methyl acrylate, MAA = methacrylic acid, MAn = maleic anhydride, MVP = 2-methyl-5-vinylpyridine, MMA = methyl methacrylate, and St = styrene; (2) for the names of organophosphorus monomers (OPM): VP = vinylphosphonate(s), MPB = monophosphonobutadiene(s), DPB = diphosphonobutadiene(s), VPA = vinylphosphonic acid $CH_2=CHP(O)(OH)_2$, DMVP = dimethyl vinylphosphonate $CH_2=CHP(O)(OCH_3)_2$, DCVP = di-β-chloroethyl vinylphosphonate $CH_2=CHP(O)(OCH_2CH_2Cl)_2$, DEVP = diethyl vinylphosphate $CH_2=CHP(O)(OC_2H_5)_2$, DEIP = 1-diethylphosphono-2-methylbuta-1,3-diene $CH_2=CH-C(CH_3)=CHP(O)(OC_2H_5)_2$, DEMOP = diethyl α-methacryloyloxymethylphosphonate $CH_2=C(CH_3)C(O)-OCH_2P(O)(OC_2H_5)_2$, DEIPO = 1-(diethylphosphine oxide)-2-methylbuta-1,3-diene 1,3-$CH_2=CH-C(CH_3)=CHP(O)(C_2H_5)_2$, DEPB = 2,3-bis(diethylphosphono)buta-1,3-diene $CH_2=C[P(O)(OC_2H_5)_2]-C[P(O)(OC_2H_5)_2]=CH_2$, TMDVP = tetramethyldiaminovinylphosphonate $CH_2=CHP(O).[N(CH_3)_2]_2$, TEDIP = 1-bisdiethylaminophosphono-2-methylbuta-1,3-diene $CH_2=CH-C(CH_3)=CHP(O)[N(C_2H_5)_2]_2$, and α-PVPA = α-phenylvinylphosphonic acid $CH_2=C(C_6H_5)-P(O)(OH)_2$.

II. MONOMERS WITH THE PHOSPHORUS ATOM AT A VINYL GROUP (TYPE A)

This class includes mainly derivatives of vinylphosphonic acid, vinylphosphines, and phosphine oxides (Table 1). The greatest amount of data has been obtained for the copolymerisation of vinylphosphonate esters.

The influence of the nature of the substituents at the phosphorus atom on the activity of VP can be traced in systems with St and VA. In relation to both polystyrene and poly(vinyl acetate) radicals, VP can be arranged in the following sequence in terms of their reactivities: DCVP > DMVP > DEVP, i.e. the reactivity of the OPM increases with the increasing electronegativity of the ester groups. The polymeric St and VP radicals add more readily to St and the poly-VA radical adds more readily to VP than to its own monomer: as a result, St is incorporated more effectively in the polymer chains than the OPM and VA and OPM have on the whole comparable reactivities in copolymerisation, but VP are nevertheless somewhat more reactive ($r_1 > r_2$).

Examination of the copolymerisation constants for the vinyl OPM together with the known copolymerisation constants for monomers without phosphorus[51] makes it possible to set up reactivity series for these monomers in relation to various macroradicals[38]. In relation to both polystyrene and poly(vinyl acetate) radicals, VP exhibit a reactivity which is intermediate between those for the conjugated (MA) and non-conjugated (VA) monomers with analogous structures. It is of interest that the reactivity of TMDVP does not differ from that of esters in relation to the polystyrene macroradical[38], which has also been noted for the addition of the phenyl radical[52].

The data in Table 1 make it possible to arrange monomers in the following sequence in terms of their reactivities with respect to the poly-DEVP radical ($1/r_1$): VA < AN < MAA < MA ≤ St < MMA. This series agrees on the whole with the series for the usual organic macroradicals[53], which shows that the behaviour of polymeric phosphorus-containing radicals in copolymerisation reactions is similar to that of ordinary macroradicals.

In addition, the copolymerisation constants together with the elementary chain propagation constants for OPM [7,8] and other monomers[53] make it possible to estimate the constants k_{21} for the addition of various radicals to the same OPM.[38] The reactivity of a phosphorus-containing macroradical may be comparable to that of the relatively inactive polystyrene

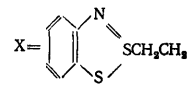
† The copolymerisation constants for the diethyl vinylphosphonate–acrylic acid system depend greatly on the nature of the solvent[33].

radical in the reaction involving addition to vinylphosphonates, while the large difference between the values of r_1 and r_2 in systems with St is almost exclusively caused by the high rate constants for the homoaddition of St and the low reactivity of VP as monomers. On the whole, some tendency towards a higher rate of addition of macroradicals to the dimethyl ester compared with the diethyl ester is observed[38].

Table 1. The copolymerisation constants for vinylphosphonic acid and its derivaties $CH_2=CHP(O)X_2$ (M_2) and the Alfrey–Price parameters.

M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
			X=HO				
St	60	0.13±0.02	24±1	0.04	[34]	—	—
MMA	60	0.09±0.01	5.6±1	0.18	[34]	1.21	0.18
AA	60	0.30±0.05	8±1	0.13	[35]	—	—
MAA	60	0.15±0.02	6±1	0.17	[35]	0.91	0.28
			X=Cl				
St	−78	0.097	1.6	0.63	[36]	0.56	0.21
MMA	−78	0.081	2.1	0.48	[36]	1.71	0.59
MMA	25	0.084	6.6	0.15	[36]	1.15	0.15
			X=CH_3O *				
St	60	0.40±0.17	4.61±0.43	0.22	[37]	—	—
St	60	0.015±0.01	5.46±0.37	0.18	[38]	0.78	0.05
VA	60	0.82±0.09	0.06±0.01	16.67	[38]	0.89	0.12
AN	—	0.09±0.02	3.55±0.18	0.28	[39]	2.31	0.51
DEVP	60	1.04±0.06	1.07±0.03	0.93	[38]	—	—
			X=C_2H_5O **				
St	—	0	3.25	0.31	[19]	—	—
St	60	0	4.40±0.50	0.24	[37]	—	—
St	60	0.06±0.02	6.32±0.34	0.16	[38]	0.19	0.07
St	—	0.06±0.02	8.87±0.14	0.11	[40]	0.01	0.21
VA	60	0.74±0.13	0.09±0.03	11.11	[38]	0.81	0.09
AA[a]	100	0.48±0.07	1.92±0.14	0.52	[33]	1.17	0.84
AA[b]	100	0.26±0.05	1.36±0.07	0.73	[33]	1.90	2.36
AA[c]	100	0.47±0.10	2.37±0.27	0.42	[33]	—	—
AA[d]	100	0.21±0.02	3.80±0.03	0.26	[33]	1.36	0.50
MA	60	0.06±0.03	6.82±0.16	0.15	[38]	1.54	0.11
AN	—	0.20±0.10	4.80±0.16	0.21	[39]	1.44	0.13
MAA	60	0.15±0.15	1.90±0.50	0.53	[41]	1.71	1.40
MMA	70	0.04±0.02	11.2±0.20	0.09	[131]	1.27	0.09
Ethylene	80	0	0.17±0.03	5.88	[42]	—	—
DMVP	60	1.07±0.03	1.04±0.06	0.94	[38]	—	—
			X=$ClCH_2CH_2O$ ***				
St	60	0.2±0.2	2.2±0.4	0.45	[43]	0.11	0.22
St	50	0.03	2.43	0.41	[44]	0.82	0.11
St	30	0.16	2.30	0.43	[45]	0.20	0.20
St	60	0.18±0.05	2.45±0.06	0.41	[38]	0.10	0.20
VA	60	0.85±0.06	0.04±0.01	25.0	[38]	1.0	0.17
MAA	60	0.10±0.08	1.7±0.5	0.59	[43]	1.92	1.78
MAA[e]	60	0.05	3.5	0.29	[46]	1.91	0.86
MAA[b]	60	0.01	4.5	0.22	[46]	1.48	0.52
MMA	30	0.26	29.9	0.03	[45]	—	—
VC	60	1.16±0.15	0.52±0.04	1.92	[47]	0.91	0.12
Ethylene	160	2.7	0.04	0.37	[48]	1.47	0.29
DEMOP	70	0.15±0.09	1.35±0.22	0.74	[49]	—	—
DEIP	70	0.15±0.08	2.12±0.04	0.47	[49]	—	—
TEDIP	70	0.10±0.10	2.0±0.4	0.50	[49]	—	—
DEIPO	70	0.06±0.06	2.86±0.10	0.35	[49]	—	—
DEPB	70	0.10±0.05	1.00±0.15	1.0	[49]	—	—
			X=C_3H_7O				
St	60	0.90±0.09	4.24±1.04	0.24	[37]	—	—
AN	40—90	0.20±0.24	4.60	0.22	[50]	1.53	0.15
			X = iso-C_3H_7O				
St	60	0	2.39±0.37	0.42	[37]	—	—
AN	40—90	0.50±0.53	4.5	0.22	[50]	—	—
			X=C_4H_9O ****				
St	60	0,3±0.3	5.4±1.5	0.19	[37]	—	—
AN	40—90	0.3—0.32	4.90	0.20	[50]	—	—
Ethylene	160	0	2.5	0.40	[48]	—	—
			X = iso-C_4H_9O*****				
St	60	0.5±0.4	4.4±1.0	0.23	[37]	—	—
AN	40—90	0.20—0.27	4.70—4.76	0.21	[50]	—	—
Ethylene	160	0	1.7	0.59	[48]	—	—
			X = iso-$C_5H_{11}O$				
AN	40—90	0.10—0.08	5.7	0.18	[50]	1.99	0.21
			X=C_6H_5O				
St	60	0	2.03±0.39	0.49	[37]	—	—
MAA[e]	60	0.13	3.5	0.29	[28]	1.48	0.67
Ethylene	80	0	0.11±0.02	9.09	[42]	—	—

Table 1. (cont.)

M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
			X = p-ClC_6H_4O				
MAA[e]	60	0.25	2.8	0.36	[28]	1 19	0.70
			X = p-$NO_2C_6H_4O$				
MAA[e]	60	0.40	1.9	0.53	[28]	1.11	1.0
			X=o-$NO_2C_6H_4O$				
MAA[e]	60	0.20	3.1	0.32	[28]	1,28	0.67
			X= 				
VC	60	0.07±0,06	3,89±0.08	0.26	[29]	1.36	0.02
			X=$(CH_3)_2N$				
St	60	0±0.02	6.20±0.24	0.16	[38]	0.65	0,05

Remarks: Solvents: [a]benzene, [b]dioxan, [c]ethyl methyl ketone, [d]water, and [e]DMF. Copolymerisation parameters and Greenley groups: $*\bar{e}_1=0.82$, $\bar{Q}_1=0.10$ (group IV, $n=5$, $R=0.92$); $**\bar{e}_1=0.92$, $\bar{Q}_1=0.074$ (group III, $n=6$, $R=0.99$); $***\bar{e}_1=1.59$, $\bar{Q}_1=0.07$ (group III, $n=7$, $R=0.91$); $****\bar{e}_1=0.62$, $\bar{Q}_1=0.03$ (group V, $n=3$, $R=0.28$); $*****\bar{e}_1=0.66$, $\bar{Q}_1=0.03$ (group V, $n=3$, $R=0.43$).

In all the systems (with the exception of AA and MAA) the parameters Q for the vinylphosphonate esters are similar and the electronegativity factors e (Table 1) vary within wide limits depending on the nature of the comonomer. For example, the shape of the curve representing the composition of the copolymers in the systems with St, MA, and MMA cannot therefore be predicted even qualitatively from the values of Q and e for the systems with VA, which is also characteristic of butyl vinylsulphonate[54], structurally similar to VP, and a number of other organoelemental monomers[55-57].

In contrast to the foregoing, when the values of $\bar{Q}$ and $\bar{e}$ obtained by the Lŭssi–Greenley method are used (Table 1), the copolymerisation constants calculated from them for VP and butyl vinylsulphonate agree qualitatively and frequently also quantitatively with the experimental values. The values of $\bar{e}$ for VP depend appreciably on the electron-accepting properties of the alkoxy-groups attached to phosphorus and there is a satisfactory linear correlation between the values of $\bar{e}$ and the Taft constants for these groups:

$$\bar{e}=1.75\sigma^*-2.05 \quad (n=5;\ R=0.986;\ s=0.07)\ .$$

This apparently provides an answer to the old question whether or not a relation exists between the capacity of VP for copolymerisation and the nature of the ester residue[37].

In terms of the resonance stabilisation factor Q, which varies from 0.03 to 0.10, VP occupy an intermediate position between typically non-conjugated monomers of the type of ethylene ($Q=0.012$ and VA($Q=0.031$), on the one hand, and conjugated monomers of the type of MA (0.44), AN (0.48), and St (1.0), on the other. For DMVP and DEVP, a linear correlation has been found between $\lg Q$ and the logarithms of the rate constants for the addition of the phenyl radical to the monomers[52]. For DEVP, a similar relation has also been observed between $\lg \bar{Q}$ and the enthalpies of activation for the thermal homolysis of azopropanes $(CH_3)_2C(X)-N=N-(X)C(CH_3)_2$, which are a measure of the energy of stabilisation of the radical by the adjacent substituent X, in the given instance $P(O)(OC_2H_5)_2$.[58] There exist also other similar correlations involving $\lg Q$ or e.[58,59]

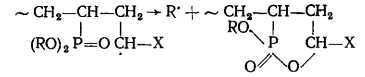
Comparison of the copolymerisation parameters of the structurally related vinyl monomers is extremely instructive (Table 2). It is seen to what extent the data for the organoelemental monomers are similar to one another and differ from those for acrylate. The similarity extends also to the styrene and vinyl acetate systems. In both cases the systems not only belong to the same type ($r_1 < 1$ and $r_2 > 1$ for St; $r_1 < 1$ and $r_2 < 1$ for VA) but are also analogous in form (the values of r_1 and r_2); both monomers have similar reactivities in relation to the macroradicals M_2 ($1/r_2$) and in terms of the alternation parameter r_1r_2. For acrylate, these systems belong to other types ($r_1 < 1$, $r_2 < 1$ and $r_1 > 1$, $r_2 < 1$ respectively) and there are differences between the systems also as regards other parameters. The values of $\bar{Q}$ and $\bar{e}$ for both organoelemental monomers indicate a low degree of conjugation and a high electronegativity. The values of $\bar{Q}$ and $\bar{e}$ for DEVP are lower than for its sulphur analogue, as was to be expected for the transition from the phosphonate to the sulphonate structure, i.e. from a Group V element to a neighbouring Group VI element on the right. The greater electron-accepting capacity of phosphonate and sulphonate compared with acrylate (judging from the values of $\bar{e}$) reflects the greater electronegativity of the metalloids on moving to the right along the Periodic System. (This relation remains valid also for all the VP in Table 1 and for all the acrylates examined by Greenley[26], with the exception of the butyl homologue).

Table 2. Comparison of the copolymerisation parameters of vinyl derivatives of carbon, phosphorus, and sulphur of the type $CH_2=CH-X$ (M_1).

X	M_2 = St				M_2 = VA				$\bar{e}_1$	$\bar{Q}_1$	Refs.
	r_1	r_2	$1/r_2$	r_1r_2	r_1	r_2	$1/r_2$	r_1r_2			
$(C_2H_5O)_2P(O)$	0.06	6.32	0.16	0.38	0.74	0.09	11	0.07	0.92	0.07	[38]
$C_4H_9OS(O)_2$	0.13	2.50	0.40	0.33	0.20	0.04	25	0.01	1.26	0.10	[26,54]
$CH_3OC(O)$	0.18	0.75	1.33	0.14	5.80	0.03	33	0.17	0.60	0.44	[26,51]

The rates of copolymerisation of VP with St, Ma, MMA, and VA decrease with increase of the content of the OPM in the system. On copolymerisation, quadratic termination of kinetic chains, usual for radical polymerisation, takes place[38]. An increase of the content of the OPM in the initial mixture and in the copolymer leads in all cases to a sharp decrease of the intrinsic viscosity and probably of the molecular weight, due to chain transfer to the OPM.[38] The determination of the constants for the chain transfer to the monomer led to the conclusion that the majority of the OPM investigated are chain transfer agents with a moderate activity. In terms of logarithmic coordinates, the constants for the chain transfer of the poly(vinyl acetate) radical to VP are satisfactorily correlated with the constants for the transfer of the same radical to the corresponding compounds of the type of POX_3 in which the vinyl group has been replaced by a third residue $X = OC_2H_5$, OC_3H_7-iso, or $N(CH_3)_2$.[60] However, the chain transfer constants themselves per group X (in the case of the monomers) are greater by 1.5–2 orders of magnitude than for POX_3.

If the chain transfer involves simply the homolytic abstraction of hydrogen, as is frequently stated in the literature[6,21] the above result can be accounted for solely by an increase of the reactivity of the hydrogen atoms in X when a single group X is replaced by a vinyl group, but we do not believe that it is possible to specify unambiguously the cause of such a radical change. Most probably the increased constants for chain transfer to the monomer are associated with the formation of relatively stable conformations of the growing ends of this chain with a greater proximity between the radical centre and the phosphoryl group of the penultimate unit, by analogy with the homopolymerisation of VP.[8,61]. In such a structure there is a possibility of intramolecular substitution leading to the abstraction of R$^\cdot$ which implies the termination of the old molecular chain and the generation of a new one without the termination of the kinetic chain (the so-called non-degradative chain transfer).



R$^\cdot$ + monomers → chain regeneration.

At any rate, there is no doubt about the significant role of the phosphoryl centre in the transfer mechanism.

The copolymerisation of VPA is of great practical interest, because it makes it possible to obtain linear, soluble, phosphorus-containing polyelectrolytes[34,35], despite the low reactivity of the monomer (Table 1).

The copolymerisation of α-PVPA has been studied in detail. In contrast to VPA,[34] this monomer does not undergo homopolymerisation[30], which was explained by the steric hindrance due to the two bulky geminal substituents. However, α-PVPA copolymerises more readily than VPA and its esters, which becomes particularly clear when the relative reactivities with respect to the polystyrene radical are compared (Table 3, the values of $1/r_2$). This is because the radical arising on addition to α-PVPA is stabilised by both substituents— the phenyl and phosphoryl groups. However, the degree of this stabilisation is greatly reduced compared with the monomer having the phenyl substituent alone, which follows directly from the copolymerisation parameters for the α-PVPA–St system[30].

Table 3. Copolymerisation parameters of α-PVPA (M_1).

M_2	t, °C	r_1	r_2	$1/r_2$	Refs	e_1	Q_1
St	70	0.20±0.05	1.50±0.05	0.67	[30]	0.30	0.28
AA	70	0.44±0.03	0.98±0.08	1.02	[63]	1.80	2.86
Acrylamide	80	0.10±0.05	2.55±0.05	0.39	[65]	—	—
AN	70	0.32±0.07	0.69±0.18	1.45	[63]	2.47	3.20
MAA	80	0.36±0.13	3.5±0.2	0.29	[62]	—	—
MMa	80	0.06±0.04	3.3±0.2	0.30	[62]	1.65	0.37
Methacrylamide	80	0	2.28±0.08	0.44	[65]	—	—
Methacrylonitrile	80	0	2.24±0.02	0.45	[64]	—	—
Chloroprene	60	0.10±0.05	7.5±0.1	0.13	[66]	1.05	0.98
2,3-Dichlorobuta-1,3-diene	—	0.07±0.01	7.75±0.10	0.13	[67]	—	—
Divinylbenzene	80	0.05±0.05	1.50±0.01	0.67	[68]	—	—

β-Phenylvinylphosphonic acid, which is isomeric with α-phenylvinylphosphonic acid, and its derivatives, which are 1,2-disubstituted ethylenes, are scarcely capable of copolymerisation and do not form copolymers with MMA and PVA. Nevertheless the constants for the copolymerisation of *trans*-$C_6H_5-CH=CH-P(O)(OC_2H_5)_2$($M_1$) with St have been determined: $r_1 = 0$ and $r_2 = 34 \pm 2$.[69]

Apart from α-PVPA, a study has also been made of the copolymerisation of other α-substituted vinylphosphonates (Table 4). The isopropenyl derivative copolymerises less

effectively than the vinyl derivative. On the other hand, the behaviour of the remaining OPM of this type on the whole occupies an intermediate position between that of the unsubstituted vinylphosphonate and the corresponding acrylates, VA, or vinyl bromide. It is of interest to compare the constants for the copolymerisation of diethyl α-acetoxyvinylphosphonate with both "parent" monomers—DEVP and VA. For the same values of r_1, the constant r_2 is appreciably smaller for VA, which reflects primarily the increase of the resonance stabilisation factor following the introduction of the phosphono-group into VA. The increase of r_2 after the introduction of the phosphono-group into vinyl bromide can be explained analogously. The copolymerisation of α-alkoxycarbonylvinylphosphonates with MMA resembles much more the behaviour of unsubstituted phosphonates than acrylates. In this instance this is a consequence of the enhancement of the electron-accepting properties of the monomer as a result of the introduction of the phosphono-group, which affects both r_1 and r_2 despite the higher values of Q for the OPM considered compared with acrylates.

Table 4. Copolymerisation parameters of the dialkyl esters of α-substituted vinylphosphonic acids $CH_2=C(X)-P(O).(OR)_2$ (M_1).[131]

M_2	t, °C	r_1	r_2	$1/r_2$	e_1	Q_1
		X=CH_3; R=CH_3 *				
St	60	0.23±0.05	8.6±0.6	0.12	—	—
MMA	60	0.2	30	0.03	—	—
VA	60	0.99±0.13	0.14±0.01	7.1	0.58	0.07
		X=$COOCH_3$; R=C_2H_5				
MMA	70	0.2	1.3	0.77	1.54	0.90
		X=$COOC_2H_5$; R=C_2H_5				
MMA	70	0.05±0.05	1.00±0.05	1.0	2.11	1.45
		X=$OCOCH_3$; R=C_2H_5 **				
St	60	0±0.05	3.88±0.37	0.26	—	—
MMA	60	0.01±0.01	4.70±0.60	0.21	1.37	0.23
VA	60	0.60±0.06	0.09±0.02	11.1	0.87	0.06
DEVP	60	0.55±0.20	0.62±0.30	1.61	1.84	0.24
		X=Br; R=C_2H_5				
MMA	70	0.04±0.04	1.25±0.15	0.80	2.11	1.16

Remarks: Copolymerisation parameters and Greenley groups: *$\bar{e}_1=1.12$, $\bar{Q}_1=0.033$ (group V, $n=3$, $R=0.95$); **$\bar{e}_1=0.51$, $\bar{Q}_1=0.076$ (group IV, $n=4$, $R=0.86$).

Vinylphosphines, vinylphosphine oxides, and vinylphosphine sulphides belong to the same type of OPM with the phosphorus atom linked directly to the vinyl group (Table 5). The relative reactivity ($1/r_2$) of diphenylvinylphosphine oxide is greater by a factor of ~3 than that of dialkylvinylphosphine oxide in copolymerisation with both St and MMA and is comparable to the reactivity of the corresponding phosphine. The latter finding is extremely remarkable. It has an analogy in the behaviour of derivatives of tricoordinate and tetra-coordinate sulphur[54,55,71], which also do not differ greatly in reactivity in copolymerisation reactions. In contrast to copolymerisation with St and MMA, where the reactivity of phosphine oxides is much lower than that of the comonomers, in the copolymerisation with VA, as in the case of VP, the reactivity of the OPM is comparable and even somewhat greater than that of VA, which leads to the appearance in the system of products with azeotropic composition.

Divinylphosphinates $(CH_2=CH)_2P(O)(OC_2H_5)$ exhibit a low reactivity in copolymerisation with MMA and St.[72]

III. MONOMERS WITH THE PHOSPHORUS ATOM AT A DIENE GROUP (TYPE B)

This group of monomers includes derivatives of butadienyl- and isopropenylphosphonic acids, butadienylenediphosphonic acids, and the corresponding phosphine oxides.

Table 5. Copolymerisation constants of vinylphosphines, vinylphosphine oxides, and vinylphosphine sulphides of the type $CH_2=CH-X$ (M_1) at 60 °C.[70]

X	M_2	r_1	r_2	$1/r_2$
$(C_6H_5)_2P$	St	0	7±1	0.14
$(C_6H_5)_2P$	MMA	0	5.1±0.2	0.20
$(C_6H_5)_2P(O)$	St	0	5±1	0.20
$(C_6H_5)_2P(O)$	MMA	0	11±4	0.09
$(C_6H_5)_2P(O)$	St	0.4±0.2	12.7±1.2	0.08**
$(C_6H_5)_2P(O)$	VA*	0.49±0.07	0.17±0.01	5.88**
$(iso\text{-}C_4H_9)_2P(O)$	St	0	17±5	0.06
$(iso\text{-}C_4H_9)_2P(O)$	MMA	0	30±10	0.03
$(C_6H_5)_2P(S)$	St	0	2.1±0.3	0.48
$(C_6H_5)_2P(S)$	MMA	0	13±3	0.08

*$e_1=0.74$; $Q_1=0.05$.

**Data of Levin et al.[38]

Table 6. Copolymerisation parameters of monophosphonobutadienes (MPB) of the type $CH_2=CH-C(CH_3)=CHP(O)X_2$ (M_1)

X	M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
Cl	St	75	1.35	0.30	3.30	[73]	0.15	0.47
F	St	75	1.15	0.54	1.90	[74]	−0.11	1.07
F	MMA	80	1.3±0.1	0.20±0.01	5.0	[75]	1.54	5.83
CH_3O	St	75	1.14±0.10	0.40±0.02	2.50	[76]	0.09	1.23
C_2H_5O	VDC	70	2.19±0.40	0.24±0.40	4.17	[77]	1.20	1.49
C_2H_5O	DCVP	70	2.12±0.04	0.15±0.08	6.70	[49]	—	—
C_2H_5O	TEDIP	70	1.22±0.12	0.09±0.01	11.1	[49]	—	—
iso-C_3H_7O	St	75	1.28±0.11	0.67±0.03	1.49	[76]	−0.41	1.09
2,4-$Cl_2C_6H_3O$	isoprene	70	0.04	0.27	3.70	[24]	1.69	3.28
$(C_2H_5)_2N$	VDC	70	0.65±0.05	0.15±0.01	6.67	[77]	1.93	3.20
$(C_2H_5)_2N$	DCVP	70	2.0±0.4	0.10±0.10	10.0	[49]	—	—
$(C_2H_5)_2N$	DEMOP	70	0.23±0.01	0.10±0.10	10.0	[49]	—	—
$(C_2H_5)_2N$	DEIP	70	0.09±0.01	1.22±0.12	0.82	[49]	—	—
$(C_2H_5)_2N$	DEPB	70	0.93±0.04	0.02±0.02	50.0	[49]	—	—
C_2H_5	VDC	70	0.58±0.01	0.08±0.04	12.5	[77]	—	—
C_2H_5	DCVP	70	2.86±0.10	0.06±0.06	16.7	[49]	—	—

Table 6 shows that, in relation to the polystyrene radical, the reactivity ($1/r_2$) of the dichloride and isopropenylphosphonic acid is higher than that of the esters and the reactivity of the latter is much higher than that of the corresponding vinylphosphonates (Table 1) and allylphosphonates (Table 10, see below). The reactivity of diene OPM is higher than that of the vinyl comonomers without phosphorus (St, MMA, and VDC). This makes it possible to obtain copolymers greatly enriched in the OPM. The sharp increase of the reactivity of the OPM of this type in copolymerisation processes is usually caused by the increase of the degree of

conjugation (Q) in the macroradicals formed following addition to the 1,4-dienes. In copolymerisation with isoprene, the products are copolymers with a rigorously alternating structure ($r_1 r_2 = 0.01$).

The study of the copolymerisation of MPB with different structures showed[77] that the reactivity of the OPM in relation to the poly-VDC radical ($1/r_2$) increases in the sequence ester < amide < oxide (Table 6). This is apparently caused by the increase of the values of e for the OPM in view of the electron-accepting nature of the VDC macroradical. An analogous behaviour has been observed also for the carboxy-radicals of the OPM.[78] The activity series established for the OPM varies in opposition to the series based on the rates of homopolymerisation of these monomers[49], i.e. in the given instance the principle of the ideal reactivity of the monomers is maintained[53].

In order to elucidate the relation between the structure and reactivity of phosphonobutadienes in radical copolymerisation with VDC, the correlation between the relative reactivity of the MPB and the electron density at the phosphorus nuclei has been examined[77]; the chemical shift ($\delta_{^{31}P}$) in the ^{31}P NMR spectra and the stretching vibration frequencies of the P=O group in the infrared spectra of the monomers investigated may serve as a measure of this reactivity within fairly narrow reaction series. Linear relations have been observed between these parameters:

$$\lg(1/r_2) = 0.34 - 0.02\,\delta_{^{31}P} \quad (R = 0.997;\ s = 0.028)$$
$$\lg(1/r_2) = 8.5 - 0.006\,\nu_{P=O} \quad (R = 0.999;\ s = 0.033).$$

As might have been expected on the basis of the values of e_1, the reactivity of MPB in relation to the electronegative poly-VDC radical increases with decrease of the stretching vibration frequencies of the phosphoryl group and as the ^{31}P NMR signals are displaced downfield, i.e. with increase of the positive charge on the phosphorus atom.

The determination of the microstructures of the polymers and copolymers by infrared and ^{31}P NMR spectroscopy showed[79] that MPB polymerise mainly in the 3,4-position, because the addition in the 1,4-position and even more so in the 1,2-position is sterically hindered owing to the presence of bulky phosphorus-containing groups. Other 1-substituted dienes with bulky silicon-, germanium-, and tin-containing groups also behave similarly in polymerisation reactions[80-82], while in the radical polymerisation of the less bulky carboxylic acid and ester analogues [$-C(O)OH$, $-C(O)OR$, and $-OC(O)CH_3$] polymers with the predominatly 1,4-structure are formed[78,83-86].

The copolymerisation of 1,3-dienes with two phosphorus atoms is of great interest from the standpoint of the modification of polymeric materials, because this process makes it possible to obtain copolymers with a higher phosphorus content but a lower fraction of OPM units and hence one can achieve the manifestation of the necessary specific properties without a significant alteration of other physicomechanical characteristics of the polymer. For this purpose, a detailed study has been made[49,77,87-89,95,132] of the radical copolymerisation of 2,3-bis[(dialkyl(aryl)]phosphonobutadienes with a whole series of vinyl and diene monomers (Table 7), which permitted a fairly complete estimate of the reactivity of these OPM in relation to different macroradicals.

For the majority of systems (with the exception of MMA, VA, and *N*-vinylpyrrolidinone), both copolymerisation constants are less than unity and $r_1 r_2 \ll 1$, i.e. the comonomers exhibit a considerable tendency towards the formation of copolymers with an alternating structure. The sequence in which the reactivity of the monomers relative to the DEPB radical ($1/r_1$) varies agrees, as for the copolymerisation of DEVP, with the analogous sequence for the majority of radicals free from phosphorus[53]: VA < AN < MMA < VDC < St < isoprene. The relative reactivity of diphosphonobutadienes with respect to the same polymeric radicals ($1/r_2$) is comparable to the reactivity of monophosphonobutadienes (Table 6) and is much higher than the reactivity of other unsaturated OPM. In particular, the reactivity of DEPB with respect to the polystyrene radical is ~20 times higher than the reactivity of DEVP (Table 1).

Table 7. Parameters of the copolymerisation of diphosphonobutadienes of the type $CH_2=C[P(O)(OR)_2]-C[P(O)(OR)_2]=CH_2$ (M_1) with 1-monosubstituted and 1,1-disubstituted ethylenes at 70 °C.

M_2	r_1	r_2	$1/r_1$	$r_1 r_2$	Refs.	e_1	Q_1
			R=C_2H_5*				
Isoprene	0±0.01	0.40±0.05	>100	<0.01	[87]	1.91	1.19
Butadiene	0±0.03	0.42±0.03	>33	<0.01	[87]	0.73	0.50
St	0.06±0.01	0.36±0.07	16.7	0.02	[88]	1.15	0.57
VDC	0.07±0.07	0.22±0.02	14.3	0.02	[77]	2.44	2.67
MMA	0.08±0.05	1.40±0.15	12.5	0,11	[88]	1.86	0.94
4-Vinylpyridine	0.08±0.02	0.40±0.05	12.5	0.03	[132]	1.77	2,22
AN	0.09±0,03	0.43±0.03	11.1	0,04	[132]	3.04	10,40
MVN	0.10±0.06	0.32±0.02	10.0	0.03	[89]	1.50	1,39
2-Vinylpyridine	0.15±0.10	0.60±0.05	6.7	0.09	[89]	1.17	1.22
N-Vinylpyrrolidinone	1.25±0.40	0.02±0.01	0.8	0,02	[132]	0.87	0.83
VA	1.85±0.50	0.05±0.05	0.5	0.09	[132]	0.70	0.17
DCVP	1.00±0.15	0.10±0.05	1.0	0.10	[49]	—	—
DEMOP	0.04±0.04	3.40±0.60	25	0.14	[49]	—	—
TEDIP	0,02±0.02	0.93±0.04	50	0.02	[49]	—	—
			R=C_6H_5				
St	0.11±0.03	0.20±0.08	9.1	0.02	[88]	1.15	1.05
MMA	0.10±0,10	1,40±0.15	10.0	0.14	[88]	1.78	0.92

*$\bar{e}_1 = 1.20$, $\bar{Q}_1 = 0.97$ (group II, $n = 9$, $R = 0.78$).

The study of the copolymerisation of styrene with DPB[88], containing ester groups at the phosphorus atom with different electronegativities, showed that the relative reactivity of DPB with respect to the polystyrene radical is described satisfactorily by the Taft equation

$$\lg(1/r_2) = 0.32\,\sigma^* - 0.08 \quad (R = 0.988;\ s = 0.028).$$

This relation shows that the reactivity of DPB esters is largely determined by the polarity of the alkoxy-groups and is independent of steric effects. The positive sign of the constant ρ^* indicates an increase of the reactivity of the monomers with respect to an electron-donating radical with increase of the electron-accepting properties of the substituents.

The reactivity of DPB with respect to the polystyrene radical is also correlated with the chemical shifts of the signals of the *trans*- and *cis*-terminal protons (in relation to the phosphono-group) in the ^1H NMR spectra and also with the stretching vibration frequencies of the phosphoryl groups of the monomers:

$$\lg(1/r_2) = 1.01\,\delta_H^{trans} - 6.05\ (R = 0.998;\ s = 0.01)\ ;$$
$$\lg(1/r_2) = 0.76\,\delta_H^{cis} - 4.33\ (R = 0.982;\ s = 0.03)\ ;$$
$$\lg(1/r_2) = 0.01\,\nu_{P=O} - 12.03 \quad (R = 0.979;\ s = 0.04).$$

The reactivity of DPB increases with increase of the chemical shifts of the protons, i.e. with decrease of the electron density in the diene system and with increase of the stretching vibration frequencies of the phosphoryl groups of the monomers. Using the relations obtained, it is possible to predict with a satisfactory accuracy the relative reactivities of phosphonobutadienes which have not yet been investigated.

Comparison of the behaviour of butadiene and DEPB in radical copolymerisation reactions with a common vinyl comonomer (Table 8) shows that the reactivity of DEPB is appreciably lower than that of butadiene (lower values of r_1). In all systems an inversion of the reactivities of the monomers can be observed, i.e. the diene becomes less reactive than the comonomer. The introduction of two phospheno-groups into the butadiene molecule reduces the reactivity of the diene system, which is caused, among other factors, by the steric hindrance due to the phosphonate groups. In terms of the relative reactivity ($1/r_2$) with respect to the macroradicals of the electron-donating type (St. MVP), DEPB is more reactive than butadiene, while with respect to electron-accepting radicals (MMA, VDC, AN), butadiene is actually more reactive than DEPB, which can be accounted for by the difference between the electronic natures of these diene monomers ($\bar{e}_{\text{butadiene}} = -1.36$; $\bar{e}_{\text{DEPB}} = 1.20$).

Table 8. Comparison of the copolymerisation constants of butadiene and DEPB.

M_2	DEPB (M_1) (Refs.88,132)		Butadiene (M_1) (Refs.51,90)	
	r_1	r_2	r_1	r_2
St	0.06	0.36	1.35	0.58
MMA	0.08	1.40	0.62	0.18
VDC	0.07	0.22	1.90	0.05
AN	0.09	0.43	0.33	0.25
MVP	0.10	0.32	1.32	0.72

From the values of $\bar{e}$ and $\bar{Q}$, DPB must be regarded as electron-accepting highly conjugated monomers. The high specific reactivities of DPB can be accounted for by the presence of the conjugated 1,3-diene system in these compounds, which ensures the effective resonance stabilisation of the resulting radicals, while the high positive values of the polarity factors are due to the presence of two electronegative phosphonate groups in the monomers. Naturally the values of $\bar{e}$ and $\bar{Q}$ for DPB are much higher than the corresponding values for monovinyl OPM. The higher reactivity of diene derivatives in copolymerisation compared with the vinyl derivatives is due largely to the higher values of Q.

Analysis of the infrared and ^{31}P NMR spectra of the monomers and polymers has shown[77,79] that, in contrast to MPB, the polymerisation of DPB proceeds preferentially in the 1,4-position. The rate of copolymerisation of DPB is proportional to the concentration of the monomers and the square root of the initiator concentration, which indicates the bimolecular termination of the polymer chains and the absence of degradative chain transfer[87,91]. In this respect phosphonobutadienes do not differ from VP.[38]

Significant differences have been observed in the study of the dependence of the rate of polymerisation and the molecular weight of the copolymers on the composition of the initial monomer mixture[25,77,87-89,91]. In the copolymerisation of DPB with MMA, AN, VDC, and certain other monomers the rate of reaction diminishes with increase of the OPM content in the initial mixture (as for VP), which is apparently caused by the replacement of the active polymeric radical derived from the vinyl monomer by the less active phosphorus-containing radical of the allyl type stabilised by conjugation. The molecular weight (intrinsic viscosity) of the copolymer also diminishes under these conditions but less markedly than the yield of the copolymer, which nevertheless makes it possible to obain high-molecular-weight polymers with a fairly high phosphorus content.

The constants for chain transfer by the poly-MMA radical to DEPB, 2,3-bis(diphenylphosphono)buta-1,3-diene, and 2,5-dimethyl-3,4-bis(diethylphosphono)hexa-2,4-diene have been determined[88] from the Mayo equation[92]. Virtually identical chain transfer constants were obtained for all three DPB, amounting to $(2.9-3.3) \times 10^{-3}$, whence it follows that the chain transfer constants depend little or not at all on the nature of the alkoxy-groups. Consequently the chain transfer reaction is not associated with the abstraction of a hydrogen atom from these groups, as for vinyl OPM,[38] since otherwise the phenyl ester would have shown a much smaller reactivity than the ethyl ester. The methyl groups in 2,5-dimethyl-3,4-bis(diethylphosphono)-hexa-2,4-diene are also not significantly involved in the chain transfer reaction, since their presence in this diene does not increase the chain transfer constant[93]. In terms of the absolute values of the chain transfer constants in the polymerisation of MMA, DPB can be characterised as chain transfer agents of moderate activity, but they are much more active than the MMA comonomer [$(0.7-1.8) \times 10^{-5}$ at 60 °C].[94]

Other features are observed in the copolymerisation of DPB with isoprene, St, vinylpyridines, and MAn, i.e. with strong electron-donating and electron-accepting conjugated monomers. In this case the dependence of the yield and the molecular weight of the copolymers on the composition of the initial monomer mixture passes through an extremum. An extremum in the yield and moleclar weight of the copolymers is observed also in many instances for MPB, particularly in the copolymerisation of bis-2,4-dichlorophenyl 2-methylbuta-1,3-dienylphosphonate with isoprene[24].

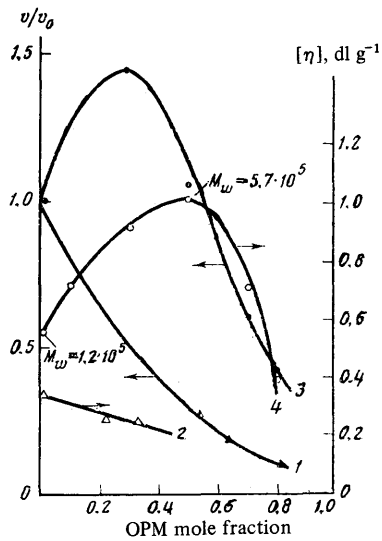
Thus organophosphorus polymers with a higher molecular weight than the corresponding purely organic homopolymers can be obtained by the copolymerisation of diene OPM with many comonomers, which constitutes an important advantage of OPM over VP in the copolymerisation of which the rate of reaction and the molecular weight of the polymers are much lower, as mentioned above. The advantages of diene OPM are clearly illustrated in the Figure, which presents the dependence of the relative rates of the process and of the molecular weight (intrinsic viscosity) of the copolymers in the copolymerisation of DEPB and DEVP with St on the composition of the initial monomer mixtures.

The tendency of phosphonobutadienes to form copolymers with an alternating structure and the extrema in the dependence of the rates of copolymerisation and the molecular weights of the copolymers on the composition of the monomer mixture may indicate[95] the formation by these OPM of charge-transfer complexes (CTC) with the comonomer.

The formation of the 1:2 CTC in the DEPB–MAn system has been demonstrated by ^1H NMR and ultraviolet spectroscopy[96]. In the copolymerisation in this system a high degree of regularity in the alternation of monomer units in the copolymer and maxima in the rate and the molecular weight of the copolymers have been observed.

The copolymerisation of DEPB with MAn in the presence of any amount of acetone, tetrahydrofuran, and acetonitrile leads to the formation of a copolymer which does not differ in composition from the polymer obtained in the absence of

these additives; however, the introduction of dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and particularly dimethylaniline into the system increases the reactivity of MAn. In terms of their influence on the reactivity of MAn, these compounds can be arranged in the sequence: DMF < DMSO ≪ dimethylaniline. This sequence is apparently caused by the decrease in the same series of the ionisation potentials of the compounds. The absence of an influence on the course of copolymerisation by other electron donors can evidently be accounted for by their inability to compete with DEPB in the donor–acceptor interaction with MAn.[96]



Dependence of the relative rates of copolymerisation v/v_0 (curves *1* and *3*) and the intrinsic viscosities of the copolymers [η] (curves *2* and *4*) on the composition of the monomer mixture in the copolymerisation of OPM with St; OPM: *1*) and *2*) DEVP; *3*) and *4*) DEPB.

With increase of the DMF concentration, r_2 increases sharply, while r_1 decreases[96,97], which indicates an appreciable increase of the reactivity of MAn in the presence of DMF. Thus the composition of the copolymers can be regulated within very wide limits by introducing electron-donating compounds into the system.

Data on the copolymerisation of DEPB with various imides of maleic acid have been published[98]. In these systems the reactivity of the monomers is independent of both the nature (DMF, dioxan) and the amount of the solvent employed. The relative reactivity of *N*-alkylmaleimides in relation to the DEPB macroradical ($1/r_1$) obeys the Taft equation:

$$\lg(1/r_1) = 0.80\,\sigma^* + 0.47 \quad (R = 0.999;\ s = 0.004)\ .$$

For *N*-arylmaleimides, a relation has been observed between the reactivity and the inductive constants σ_I of the substituents in the aryl residue:

$$\lg(1/r_1) = 0.46\,\sigma_I + 1.3 \quad (R = 0.990;\ s = 0.022)\ .$$

A study of the copolymerisation of allene OPM–diethyl and dibutyl 3-methylbuta-1,2-dienylphosphonates—with MA (M_2) established[99] that the allene derivatives of phosphorus are characterised by a low reactivity ($r_1 = 0$, $r_2 \gg 1$).[99] The replacement of the diene group by the allene group reduces sharply the copolymerisation capacity of the OPM, which was in fact to be expected in view of the absence of conjugation in the π-electron system of the allene group.

IV. MONOMERS WITH THE PHOSPHORUS ATOM IN THE β- OR γ-POSITION RELATIVE TO A VINYL GROUP (TYPE C)

Vinyl and allyl phosphates and vinyl- and allyl-phosphonates should be included in this group of monomers. It follows from Table 9 that vinyl phosphates copolymerise much more readily with structurally analogous vinyl esters than with St. The reactivity of vinyl phosphates in copolymerisation with St is very low and in practice only the St homopolymer is formed. The relative reactivity of vinyl phosphates in reactions with macroradicals is much lower, as was to be expected (by analogy with carboxy-analogues), than the reactivity of VP and is comparable to the reactivity of VA. The quantities Q and $\bar{Q}$ are on the whole lower than for VP, i.e. the introduction of oxygen between the vinyl group and phosphorus reduces the conjugation between the vinyl group and the phosphorus-containing residue which was in any case already low. This is also evident from the behaviour of diethylvinyl phosphate in relation to C_6H_5.[52] The copolymerisation with MAn likewise resembles the behaviour of VA and is characterised by a high degree of regularity in the alternation of units.

Table 9. Copolymerisation parameters of vinyl phosphates of the type $CH_2=CH-O-P(O)(OR)_2$ (M_1) at 60 °C.

M_2	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
			R=CH_3			
St	0±0.1	23.0±5.0	0.04	[38]	—	—
VA	0.19±0.04	1.28±0.06	0.78	[38]	−2.03	0.01
			R=C_2H_5 *			
St	0.04±0.10	91±30	0.01	[38]	—	—
VA	0.25±0.09	1.59±0.10	0.63	[38]	−1.80	0.04
Vinyl chloroacetate	0.43	2.0	0.50	[100]	−1.04	0.07
VC	0.20	3.3	0.30	[100]	−0.44	0.02
MAn	0	0.2	5.0	[100]	—	—
			R=C_6H_5			
Vinyl chloroacetate	0.50	1.4	0.71	[100]	−0.83	0.02
VC	0.25	2.8	0.36	[100]	−0.40	0.02
MAn	0	0.2	5.0	[100]	—	—

*$\bar{e}_1 = -3.04$, $\bar{Q}_1 = 0.06$ (group IV, $n = 4$, $R = 0.84$).

There have been many communications on the copolymerisation of allyl derivatives of phosphorus[5,101], but the majority of the investigators restricted themselves to the determination of the phosphorus content in the copolymers and to estimating some of their properties. The available quantitative data on the compolymerisation of monoallyl derivatives of phosphorus are presented in Table 10. In terms of their ability to react with the poly-MAA radical, the monomers listed in Table 10 can be arranged in the sequence DEVP > diethyl allylphosphonate > 1,4-bis(diethylphosphono)-but-2-ene[102]. This sequence in the variation of the reactivities

is associated with the decrease of Q on passing from the vinyl to the allyl monomer (rupture of the conjugation chain) and with the transition from the mono- to the 1,2-disubstituted ethylene; the latter always causes a sharp reduction in the reactivity of monomers. Allyl derivatives of phosphorus exhibit a lower reactivity in copolymerisation with unsaturated polyesters[104,105].

Table 10. Parameters of the copolymerisation of allyl derivatives of phosphorus.

M_1	M_2	t, °C	r_1	r_2	$1/r_2$	Refs.	e_1	Q_1
$CH_2=CHCH_2P(O)(OCH_3)_2$	AN	—	0.05±0.02	4.70±0.18	0.21	[39]	2.44	0.45
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	MAA	60	0.04±0.04	6.1±0.4	0.17	[102]	1.79	0.15
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	DMA	80	0.07	52.5	0.02	[103]	—	—
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	AN	—	0	4.30±0.18	0.23	[39]	—	—
$CH_2=CHCH_2P(O)(OC_2H_5)_2$	PBGF*	80	0.12±0.08	9.25±3.00	0.11	[104]	—	—
$CH_2=CHP(O)(OC_2H_5)_2$	MAA	60	0.15±0.15	1.9±0.5	0.53	[102]	1.72	0.45
$CH_2-CH=CH-CH_2$ $P(O)(OC_2H_5)_2$ $P(O)(OC_2H_5)_2$	MAA	60	0±0.10	12.0±1.0	0.08	[102]	—	—
$CH_2=CHCH_2OP(H)(=O)OC_2H_5$	PBGF	80	0.03±0.03	5.5±2.5	0.18	[105]	—	—

*PBGF = poly(1,3-butylene glycol fumarate).

Table 11. Copolymerisation constants of diallyl OPM.

M_1	M_2	t, °C	r_1	r_2	$1/r_2$	Refs.
$(CH_2=CHCH_2O)_2P(O)C_2H_5$	DMA	80	0.09	18.7	0.05	[103]
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	DMA	80	0.07	19.5	0.05	[103]
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	MMA	70	0.14	22.96	0.04	[106]
$(CH_2=CHCH_2O)_2P(O)C_6H_5$	St	70	0.03	28.97	0.03	[106]
$(CH_2=CHCH_2O)_2P(O)(OC_6H_4)$	MMA	70	0.22	9.78	0.10	[107]
$(CH_2=CHCH_2O)_2P(O)(OC_6H_4)$	St	70	0.15	16.84	0.06	[107]
$[(CH_2=CHCH_2O)_2P=N]_3$	St	70	0.22	0.51	1.96	[108]
$(CH_2=CHCH_2)_2P(O)C_6H_5$	DMA	80	−0.01±0.01	18.1±0.4	0.06	[109]
$(CH_2=CHCH_2)_2P(O)C_6H_5$	DMA	110	−0.01±0.02	11.1±0.4	0.09	[109]
$(CH_2=CHCH_2)_2P(O)C_6H_5$	DMA	140	−0.09±0.02	5.59±0.24	0.18	[109]

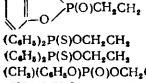
A number of studies[103,106–109] have been devoted to the copolymerisation of diallyl OPM (Table 11), which copolymerise via both allyl groups with formation of cyclolinear polymers, which is indicated by the lower degree of unsaturation and the high solubility of the products. Table 11 shows that phosphonates are relatively inactive monomers. The relative reactivities of butyl- and phenyl-phosphonates are the same, i.e. the presence of acid groups does not influence the reactivity of the monomers which is apparently due to the remoteness of these groups from the double bond. On passing to the phosphates, the reactivity of the OPM increases somewhat. The reactivity of diallyl derivatives of phosphorus with respect to the polymeric methacrylate radicals is approximately the same regardless of their structure and somewhat higher than the reactivity of allyl OPM (Table 10). With increase of temperature, the reactivity of the OPM with respect to the poly-DMA radical increases. It is believed[109] that the negative values of r_1 are due to the influence of the penultimate unit but one cannot rule out the possibility that other factors also operated, since the experiments were performed at fairly high temperatures where there is a possibility of depolymerisation and of other processes.

The copolymerisation of diallyl methylphosphonate with ethylene[110], in contrast to the copolymerisation with MMA and St, involves one of the allyl bonds. Since the copolymerisation was carried out[110] at low OPM concentrations, only the constant r_2 can be determined with an adequate accuracy. It decreases with increasing pressure, while r_1 is stated by the author to lie in the range between 0 and 2.

V. MONOMERS WITH THE PHOSPHORUS ATOM REMOTE FROM A VINYL GROUP (TYPE D)

This class of OPM includes mainly substituted acrylates, methacrylates, and styrene derivatives. They copolymerise almost in the same way as the analogous monomers without phosphorus. Data on the copolymerisation of phosphonoacrylates with vinyl monomers are presented in Table 12, from which it follows that phosphonoacrylates enter into the composition of the copolymer with somewhat more difficulty than MA and MMA, while in the copolymerisation with St their reactivities are comparable, i.e. the copolymerisation resembles that in the MMA–St system. Naturally the ability of phosphonoacrylates to combine with macroradicals is much greater than that of VP, which makes it possible to obtain polymers with a high phosphorus content. The factors Q and e for phosphonoalkyl methacrylates are frequently close to the corresponding parameters for MMA.

Table 12. Copolymerisation parameters of methacryloyl derivatives of phosphorus $CH_2=C(CH_3)COOR$ (M_1).

R	M_2	t, °C	r_1	r_2	Refs.	e_1	Q_1
$(C_6H_5O)_2P$	St	60	0.09±0.01	2.08±0.01	[111]	0.49	0.17
$(C_6H_5O)_2P$	MMA	60	0.05±0.01	3.97±0.01	[111]	—	—
$(C_6H_5O)_2P(O)$	St	60	0.01±0.01	0.32±0.01	[111]	1.60	0.46
$(C_6H_5O)_2P(O)$	MMA	60	0.11±0.01	0.70±0.01	[111]	—	—
$(BrCH_2CH_2O)(C_6H_5O)P(O)$	AN	40	2.20	0.27	[113]	1.96	4.34
$(C_2H_5O)_2P(O)CH_3$ *	MA	75	0.29±0.05	0.88±0.09	[114]	1.77	1.01
$(C_2H_5O)_2P(O)CH_3$ *	MMA	75	0.27±0.01	1.88±0.03	[114]	1.20	0.55
$(C_2H_5O)_2P(O)CH(CH_3)_2$ *	MMA	65	0.15±0.03	2.02±0.05	[114]	1.47	0.56
$(C_2H_5O)_2P(O)CH_3$	MMA	68	0.50±0.03	1.43±0.05	[114]	0.96	0.65
$(C_2H_5O)_2P(O)CH_3$	VDC	70	1.50±0.15	0.40±0.06	[132]	1.12	0.87
$(C_2H_5O)_2P(O)CH_3$	DCVP	70	1.35±0.22	0.15±0.09	[49]	—	—
$(C_2H_5O)_2P(O)CH_3$	GEDIP	70	0.10±0.01	0.23±0.01	[49]	—	—
$(C_2H_5O)_2P(O)CH_3$	DEPB	70	3.40±0.60	0.04±0.04	[49]	—	—
$(CH_3O)_2P(O)CH_2CH_3$	St	80	0.49±0.03	0.37±0.02	[115]	0.51	0.95
$(C_2H_5O)_2P(O)CH_2CH_3$	St	80	0.45±0.02	0.39±0.02	[115]	0.52	0.89
$(C_4H_9O)_2P(O)CH_2CH_3$	St	80	0.35±0.01	0.46±0.02	[115]	0.55	0.74
 $P(O)CH_2CH_3$	St	80	0.55±0.02	0.34±0.01	[115]	0.49	1.04
$(C_6H_5)_2P(S)OCH_2CH_3$	St	70	0.38	0.47	[116]	0.51	0.73
$(C_6H_5)_2P(S)OCH_2CH_3$	MMA	70	0.45	0.88	[116]	1.35	1.24
$(CH_3)(C_6H_5O)P(O)OCH_2C_6H_5$	St	70	0.31	0.50	[117]	0.56	0.67
$(CH_3)(C_6H_5O)P(O)OCH_2CH_3$	MMA	70	0.43	0.49	[117]	1.63	2.46
$(CF_3)(C_6H_5O)P(O)OCH_2CH(Cl)$	St	70	0.07±0.01	2.00±0.05	[117]	0.60	0.16
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)$	MMA	70	0.01±0.01	1.51±0.05	[118]	2.43	1.08
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)$	St	70	0.14±0.01	1.10±0.05	[119]	0.57	0.30
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	St	70	0.12±0.01	3.36±0.05	[118]	0.15	0.14
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	MMA	70	0.30±0.02	1.61±0.05	[118]	1.23	0.64
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	MMA	70	0.45±0.05	0.86±0.05	[119]	1.35	1.26
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	VDC	70	0.14±0.01	0.85±0.05	[119]	1.85	0.54
$(CH_3)(C_6H_5O)P(O)OCH_2CH(Cl)CH_3$	butyl acrylate	70	0.27±0.01	0.97±0.05	[119]	1.90	0.73
$(C_6H_5)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	St	70	0.39±0.01	1.87±0.05	[118]	0.24	0.34
$(C_6H_5)(C_6H_5O)P(O)OCH_2CH(Cl)CH_2$	MMA	70	0.26±0.02	1.37±0.05	[118]	1.40	0.81
$(CH_3)(C_6H_5O)P(O)OCH_2CH(OH)CH_2$	St	70	0.04±0.01	1.99±0.10	[119]	0.79	0.14
$(C_2H_5O)_2P(O)OCH_2CH(Cl)CH_2$	St	60	0.37±0.01	0.64±0.08	[120]	0.40	0.60
$(C_2H_5O)_2P(O)OCH_2CH(Cl)CH_2$	MMA	60	0.73±0.03	1.20±0.13	[120]	0.74	0.72
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_2$	St	60	0.22±0.03	0.47±0.02	[120]	0.71	0.64
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_2$	MMA	60	0.57±0.01	0.81±0.01	[120]	1.26	1.30
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_2$	St	60	0.65±0.04	0.22±0.04	[120]	0.60	1.50
$(C_6H_5O)_2P(O)OCH_2CH(Cl)CH_2$	MMA	60	0.33±0.03	0.76±0.05	[120]	1.56	1.55

*Acryloyl derivatives.

Examination of data for the copolymerisation of phosphonoalkyl methacrylates with St (Table 12) shows that the nature of the phosphorus-containing group nevertheless does exert some influence on the reactivity of these monomers, but the nature of this influence is not clear. We can only note that the higher electronegativity of the diphenyl phosphate group compared with the phosphite group also leads to a greater reactivity of methacryloyl phosphate also in relation to the polystyrene radical, compared with methacryloyl phosphite[111]. At the same time vinylphosphines and *p*-styrylphosphines have virtually the same copolymerisation constants as their oxides. This behaviour of the methacryloyl derivatives in cases where the influence of the environment of the phosphorus should be manifested to an even lesser extent requires further experimental confirmation particularly since methacryloyl phosphates are thermally unstable[112]

Styrenes with phosphorus-containing groups in the ring belong to monomers of the same type. The copolymerisation of the chloride and the dibutyl ester of *p*-styrylphosphonic acid with certain monomers has been investigated[121]. On the basis of the available data for the compositions of the copolymers and the initial mixtures, one may conclude that the ester is much more reactive than VA in copolymerisation while the acid chloride has a reactivity comparable to those of St and MMA.

The study of the copolymerisation of the styrenes listed in Table 13 [122,123] showed that these monomers are more reactive than St and MMA and that $r_1 > 1$ and $r_2 < 1$. This makes it possible to obtain copolymers greatly enriched in the OPM over the entire range of initial compositions. It is of interest that Q increases following the introduction of phosphorus-containing groups in St, evidently as a result of their inclusion in the conjugation chain. The quantity e also naturally increases as a result of the introduction of electronegative phosphorus-containing groups. It follows from Table 13 that the relative reactivities of both phosphine (P^{III}) and phosphine oxide and sulphide (P^{IV}) are virtually the same. The similar influence of groups with P^{III} and P^{IV} on the reactivity of the double bond in OPM of type A was noted above but, as already stated, the situation is different for methacrylates.

Table 13. Copolymerisation parameters of diphenyl-*p*-styrylphosphine, its oxide, and its sulphide of the type $CH_2=CH-C_6H_4-X$ (M_1). [123]

X	M_2	t, °C	r_1	r_2	$1/r_2$	e_1	Q_1
$(C_6H_5)_2P$ *	St	65	1.11±0.12	0.46±0.07	2.17	+0.02	1.13
$(C_6H_5)_2P$	St	60	1.43±0.25	0.52±0.05	1.92	−0.30	1.25
$(C_6H_5)_2P$	MMA	60	0.91±0.12	0.32±0.02	3.13	−0.73	1.54
$(C_6H_5)_2P(O)$	St	60	1.40±0.15	0.42±0.02	2.38	−0.07	1.34
$(C_6H_5)_2P(O)$	MMA	60	1.46±0.10	0.38+0.02	2.63	−0.39	1.47
$(C_6H_5)_2P(S)$	St	60	1.49±0.33	0.43±0.05	2.33	−0.13	1.37
$(C_6H_5)_2P(S)$	MMA	60	1.22±0.34	0.29±0.01	3.45	−0.64	1.76

*According to the data of Braun et al. [122]

The data presented in Table 13 on the copolymerisation of styrenes substituted with phosphorus-containing groups in the *p*-position are described satisfactorily by the familiar[124,125] linear relation between the relative reactivity of the styrene monomers with respect to the polystyrene radical and the Hammett constants. The σ constants of the substituents taken from Tsvekov and coworkers[126,127] were used:

$$\lg(1/r_1) = 0.57\sigma + 0.14 \quad ,$$

i.e. phosphorus-containing styrenes obey the same relations as other *p*-substituted styrenes.

The styrene derivatives of arsenic, antimony, and bismuth with structures analogous to that of diphenyl-*p*-styrylphosphine exhibit the same reactivity as the phosphine in copolymerisation with St. [122]

VI. COPOLYMERISATION OF ORGANOPHOSPHORUS MONOMERS OF DIFFERENT TYPES

Direct comparison of the reactivities of different types of OPM in their copolymerisation with one another is of interest[49]. (see Tables 1,6, and 12). Table 1 shows that acrylic and diene OPM have much higher reactivities than VP.

In the copolymerisation of diene OPM the ester of isoprenylphosphonic acid is more reactive than the amide (Table 6), as has been observed also for acrylic acid derivatives[128], and MPB are more reactive than DPB (Table 6). Phosphonoalkyl methacrylates have an activity comparable to that of monophosphonobutadienes, but higher than that of diphosphonobutadienes (Table 12). The reactivity of MPB with respect to the electronegative DCVP macroradical (Table 6) increases, like that with respect to the poly-VDC radical[77], with decrease of the stretching vibration frequencies of the phosphoryl group and with increase of the negative chemical shifts $\delta_{^{31}P}$:

$$\lg(1/r_2) = 0.59 - 0.02\,\delta_{^{31}P} \quad (R = 0.995;\ s = 0.028)$$

$$\lg(1/r_2) = 7.1 - 0.005\,\nu_{P=O} \quad (R = 0.993;\ s = 0.033).$$

The reactivity of phosphonoalkyl methacrylate with respect to the poly-DCVP radical ($1/r_2$) is comparable to that of isoprenylphosphonate but somewhat lower than the reactivity of butadienylenediphosphonate (Table 1), in agreement with data for the copolymerisation of these monomers with St[76,88,115].

Table 14. The relative reactivities ($1/r_2$) of organophosphorus monomers (M_1) with respect to the polystyrene radical.

OPM	$1/r_2$	Refs.
$CH_2=CH-C(CH_3)=CHP(O)Cl_2$	3.33	[73]
$CH_2=C[P(O)(OC_2H_5)_2]-C[P(O)(OC_2H_5)_2]=CH_2$	2.80	[88]
$CH_2=C(CH_3)C(O)OCH_2CH_2P(O)(OC_2H_5)_2$	2.56	[115]
$CH_2=CH-C(CH_3)=CHP(O)(OCH_3)_2$	2.50	76]
$CH_2=CH-C_6H_4-P(O)(C_6H_5)_2$	2.38	[123]
$CH_2=CH-C_6H_4-P(S)(C_6H_5)_2$	2.33	[123]
$CH_2=C(CH_3)C(O)OCH_2CH_2OP(S)(C_6H_5)_2$	2.14	[116]
$CH_2=CH-C_6H_4-P(C_6H_5)_2$	1.92	[123]
$CH_2=C(CH_3)C(O)OCH_2CHCH_2OP(O)(OC_2H_5)_2$	1.56	[120]
$CH_2=C(C_6H_5)-P(O)(OH)_2$	0.67	[30]
$CH_2=CH-P(O)(OC_6H_5)_2$	0.49	[37]
$CH_2=CH-P(O)(C_6H_5)_2$	0.20	[70]
$CH_2=CH-P(O)(OC_2H_5)_2$	0.16	[38]
$CH_2=CH-P(O)[N(CH_3)_2]_2$	0.16	[38]
$CH_2=CH-P(C_6H_5)_2$	0.14	[70]
$(CH_2=CHCH_2O)_2P(O)(OC_6H_5)$	0.06	[107]
$CH_2=CH-P(O)(OH)_2$	0.04	[34]
$(CH_2=CHCH_2O)_2P(O)(C_6H_5)$	0.03	[106]
$CH_2=CHOP(O)(OC_2H_5)_2$	0.01	[38]

VII. CONCLUSION

It is of interest to examine the reactivities of OPM of different types and with different structures in relation to the standard polystyrene radical (Table 14). Evidently the reactivity of OPM varies within very wide limits: the reactivities of the first and last OPM differ by more than two orders of magnitude. This reactivity series is apparently on the whole analogous to the series for other polymeric radicals, as can be seen from Table 15, which presents the reactivities of the most thoroughly investigated OPM with respect to various macroradicals. The behaviour of new OPM can be assessed and the most promising of these can be selected on the basis of similar series.

Table 15. The relative reactivities ($1/r_2$) of OPM (M_1) in reactions with various polymeric radicals

OPM	St [38, 76, 88, 115]	MMA [45, 88, 114]	VDC [77, 132]	VA [38, 132]	VC [47]
$CH_2=C[P(O)(OC_2H_5)_2]-C[P(O)(OC_2H_5)_2]=CH_2$	2.80	0.71	4.55	20.0	—
$CH_2=CH-C(CH_3)=CHP(O)(OR)_2$	2.50*	—	4.17**	—	—
$CH_2=C(CH_3)-C(O)O-(CH_2)_n-P(O)(OC_2H_5)_2$	2.56***	0.70****	2.50****	—	—
$CH_2=CHP(O)(OCH_2CH_2Cl)_2$	0.41	0.03	0.49	25.0	1.92

* $R = CH_3$. ** $R = C_2H_5$. *** $n = 2$. **** $n = 1$.

Tables 14 and 15 show that diene, methacrylate, and styrene derivatives of phosphorus are most suitable for the modification of polymers by the copolymerisation method. However, the synthesis of the last two types of monomers is extremely laborious, the latter being obtained in low yields and frequently with a low purity. Furthermore, the presence of bulky side groups in the chain at the phosphorus atom greatly reduces the thermal stability of copolymers based on them[129,130].

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As can be seen from the foregoing, the method of the copolymerisation of unsaturated OPM can be used successfully to modify a wide variety of polymeric materials. By altering the nature and the structure of OPM, it is possible to vary widely both the rate of the process and the molecular weights of the products, on the one hand, and the composition of the copolymers and ultimately the properties of the polymers in the desired manner, on the other.

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