General Conclusions about the Copolymerization of Ethylene with Other Monomers by Free Radical Catalysis

FRANCIS E. BROWN and GEORGE E. HAM, *Spencer Chemical Company, Research Center, Merriam, Kansas*

Synopsis

The behavior of ethylene in copolymerization with methyl acrylate, methyl methacrylate, vinyl acetate, diethyl fumarate, and diethyl maleate was investigated, and reactivity ratios for these systems reported. Significant deviations of all systems investigated, except ethylene–vinyl acetate, from the conventional copolymerization equation are noted and interpreted on the basis of substantial penultimate and penpenultimate effects. The consistency of the reactivity ratios developed in the systems ethylene–methyl acrylate and ethylene–methyl methacrylate with reported values for methyl acrylate–methyl methacrylate is shown by application of the relationship $P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba}$.

The copolymerization of ethylene with various monomers, polar and nonpolar, by free radical catalysis has been previously reported.[1,2] Mortimer and co-workers investigated the copolymerization of ethylene (M_1) and propylene (M_2), analyzed the products by a C^{14} tracer technique, and reported reactivity ratios $r_1 = 3.30 \pm 0.15$ and $r_2 = 3.1 \pm 1.7$. An $r_1 r_2$ product of 10.2 was obtained.

These results create new questions about the physical nature of ethylene copolymerization as compared with most other free radical copolymerizations. The prospect of block-type copolymerizations (preferred addition of either radical to its own monomer arising from $r_1 r_2 > 1$) is difficult to explain in the light of present knowledge of the nature of free radical copolymerization in homogeneous phase. In addition, ethylene monomer possesses a "duality" in copolymerization not shared by any other monomer. Either end may add equally well to growing radicals, which could lead to higher effective concentrations in copolymerization.

Zutty and Burkhart[2] reported copolymerizations of ethylene with *n*-butyl acrylate, vinyl chloride, vinyl acetate, and vinyl fluoride at 1000 atm. Their studies showed, on the contrary, reactivity ratio products $(r_1 r_2)$ equal to unity within experimental error for the last three systems and equal to 0.36 ± 0.12 for ethylene–*n*-butyl acrylate. The last result would indicate an appreciable alternating tendency in this system, but for the fact that r_1 (ethylene $= M_1$) $= 0.03$. Such a low value cannot be determined with great precision, so the most that can be concluded is that some tendency

TABLE I

Run no.	Monomer	Feed						Product					
		M_2, moles	M_1, moles	M_1/M_2	$\frac{M_1}{M_1+M_2}$	$\frac{M_2}{M_1+M_2}$	m_2, wt.-%	m_2, moles	m_1, moles	m_1/m_2	m_2/m_1	$\frac{m_1}{m_1+m_2}$	$\frac{m_2}{m_1+m_2}$
1308	Vinyl acetate	0.031	3.64	117.4	0.992	0.008	1.82	0.0211	3.51	166.3	0.006	0.994	0.006
1307	Vinyl acetate	0.153	3.47	22.7	0.961	0.039	11.18	0.130	3.17	24.4	0.041	0.961	0.039
1309	Vinyl acetate	1.68	1.37	0.815	0.688	0.312	60.75	0.706	1.40	1.98	0.504	0.665	0.335
1256	Methyl acrylate	0.031	3.64	117.4	0.992	0.008	12.51	0.145	3.26	22.5	0.041	0.957	0.043
1255	Methyl acrylate	0.153	3.49	22.8	0.961	0.039	48.30	0.562	1.85	3.29	0.304	0.767	0.233
1333	Methyl acrylate	2.00	1.29	0.645	0.393	0.607	97.4	1.145	0.0929	0.0811	12.3	0.0750	0.925
1334	Methyl acrylate	2.00	1.22	0.610	0.379	0.621	99.1	1.150	0.0321	0.028	35.82	0.027	0.973
1276	Diethyl fumarate	0.306	2.94	9.6	0.925	0.075	65.4	0.380	1.24	3.26	0.306	0.765	0.235
1277	Diethyl fumarate	0.153	3.31	21.6	0.969	0.031	23.11	0.134	2.75	20.52	0.049	0.954	0.046
1279	Diethyl fumarate	0.84	1.66	1.97	0.815	0.185	80.9	0.470	0.68	1.42	0.691	0.591	0.409
1429	Diethyl fumarate	1.0	1.28	1.28	0.562	0.438	96.0	0.557	0.143	0.257	3.895	0.204	0.796
1429	Diethyl fumarate	1.0	1.28	1.28	0.562	0.438	95.5	0.554	0.160	0.289	3.463	0.224	0.776
1430	Diethyl fumarate	1.0	1.21	1.21	0.547	0.453	91.4	0.530	0.307	0.579	1.726	0.367	0.633
1432	Diethyl fumarate	1.0	1.00	1.00	0.500	0.500	99.0	0.574	0.0356	0.062	16.123	0.058	0.942
1282	Methyl methacrylate	0.031	3.63	117.0	0.992	0.008	13.4	0.134	3.09	23.0	0.043	0.958	0.042
1281	Methyl methacrylate	0.153	3.44	22.8	0.961	0.039	15.2	0.152	3.03	19.9	0.050	0.952	0.048
1283	Methyl methacrylate	0.84	2.39	2.84	0.815	0.185	86.8	0.867	0.471	0.543	1.84	0.352	0.648
	Methyl methacrylate	1.53	1.295	0.846	0.458	0.541	98.4	0.984	0.057	0.058	17.2	0.0547	0.944
1274	Diethyl maleate	0.031	3.61	116.4	0.992	0.008	16.11	0.093	2.99	32.15	0.031	0.971	0.029
1275	Diethyl maleate	0.84	1.69	2.01	0.815	0.185	86.21	0.501	0.49	0.978	1.02	0.494	0.506

toward alternation exists. Unfortunately, no compositions were reported containing more than 55 wt.-% ethylene, so no firm conclusions about $r_1 = K^{aaa}/K^{aab}$ can be drawn. A similar difficulty in assessing $r_1 = K^{aaa}/K^{aab}$ for the system ethylene (M_1)–vinyl chloride (M_2) exists, since no compositions containing more than 40 wt.-% ethylene were reported. Their conclusions about ethylene–vinyl acetate do not suffer from this limitation. However, data at low vinyl fluoride contents in the system ethylene (M_1)–vinyl fluoride (M_2) raise substantial doubts about the reported r_1 value (4.39 ± 0.77) and suggest possibly large differences among K^{aaaa}/K^{aaab}, K^{baaa}/K^{baab}, and K^{baa}/K^{bab}.

In our study, ethylene has been copolymerized with vinyl acetate, methyl acrylate, methyl methacrylate, diethyl maleate, and diethyl fumarate at 150°C. and pressures of 12,000 psi (Table I).

The calculated reactivity ratios for the best fit of the conventional co-polymer composition equation are given in Table II.*

TABLE II
Reactivity Ratios

M_1	M_2	r_1	r_2	r_1r_2
Ethylene	Vinyl acetate	1.01	1	1
Ethylene	Methyl acrylate	0.2	11	2.2
Ethylene	Methyl methacrylate	0.2	17	3.4
Ethylene	Diethyl maleate	0.25	10[a]	2.5[a]
Ethylene	Diethyl fumarate	0.25	10	2.5

[a] The value for r_2 in this system raises questions because of the experimental difficulties of producing copolymer at high levels of diethyl maleate. Other systems such as VAc–diethyl maleate would suggest that this r_2 value may be lower. Our higher operating temperatures, however, would tend to increase r_2.

The fitting of data to the conventional equation unfortunately leads to a theoretical curve in the case of ethylene–methyl acrylate which is substantially divergent from experimental points (Fig. 1) particularly at high ethylene proportions in the charge. By employing Barb's equation,[3] where penultimate effects can be assessed:

$$n - 1 = r_1' x (r_1x + 1)/(r_1' x + 1) \qquad (1)$$

where $x = A/B$ the ratio of monomers in the charge, $n = a/b$ the ratio of monomers in the copolymer, and

$$r_1 = K^{aaa}/K^{aab}$$
$$r_1' = K^{baa}/K^{bab}$$

would be possible if addition of methyl acrylate to methyl acrylate free radical were unimportant at higher ethylene concentrations. However, since $r_2 = 11$, the more precise equation[4] is required.

* The copolymer compositions were determined by calibrated infrared techniques devised by Dr. R. H. Hughes.
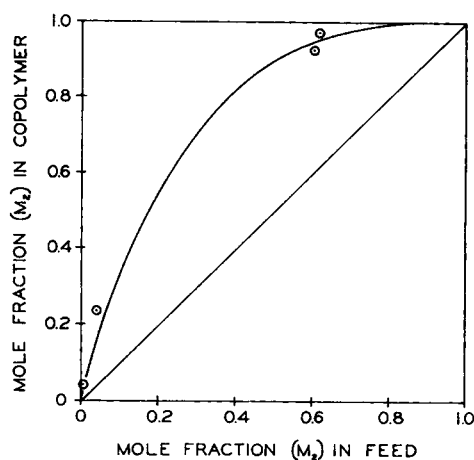
Fig. 1. Ethylene–methyl acrylate copolymerization.

$$\frac{a}{b} = \frac{[r_1' \, x \, (r_1 \, x + 1)/(r_1' \, x + 1)] + 1}{(r_2/x) + 1} \qquad (2)$$

It was found that the latter equation fitted the data well with $r_1 = 0.30$, $r_1' = 0.15$, and $r_2 = 11$.

The importance of the contribution to composition of additions of methyl acrylate monomer to methyl acrylate radical at various ethylene–methyl acrylate ratios is shown in the comparison given in Table III.

TABLE III

Monomer ratio $x(M_1/M_2)$	Copolymer ratio $n(m_1/m_2)$		
	Barb's equation	Eq. (2)	Experimental curve
49	14.8	12.1	11.5
24	7.4	5.08	6.15
15.7	5.0	2.94	3.76
5.0	2.075	0.65	0.85

A comparison of predictions of the conventional copolymer equation ($r_1 = 0.20$, $r_2 = 11$), eq. (2) ($r_1 = 0.30$, $r_1' = 0.10$, $r_2 = 11$), and the preferred eq. (2) ($r_1 = 0.30$, $r_1' = 0.15$, $r_2 = 11$) with experimental values is shown in Table IV.

It is of interest that, whereas (for $r_1 = 0.30$, $r_1' = 0.15$, $r_2 = 11$) $r_1r_2 = 3.3$, $r_1'r_2 = 1.65$. The latter result indicates a tendency toward random addition in copolymerization at other than high ethylene proportions. Our conclusions about $r_1'(K^{baa}/K^{bab})$ suffer from lack of data in the intermediate range.

TABLE IV

Monomer Ratio $x(M_1/M_2)$	Copolymer ratio $n(m_1/m_2)$			
	Conventional copolymer eq. $(r_1 = 0.2,$ $r_2 = 11)$	Eq. (2) $(r_1 = 0.30,$ $r_1 = 0.10,$ $r_2 = 11)$	Eq. (2) $(r_1 = 0.30,$ $r_1 = 0.15,$ $r_2 = 11)$	Experimental curve
49	8.8	11.4	12.1	11.5
24	3.97	4.67	5.08	6.15
15.7	2.85	2.65	2.94	3.76
5	0.625	0.592	0.65	0.85
1	0.10	0.093	0.098	0.124

A related, but rather different situation exists in the system ethylene–methyl methacrylate (Fig. 2). The best fit of the data with the conventional copolymer equation leads to $r_1 = 0.2$ and $r_2 = 17$. A remarkable $r_1r_2 = 3.4$ results. Such values do not give proper weight to low methyl methacrylate contents in copolymers in the intermediate regions.

Thus, a mole fraction of 0.721 methyl methacrylate in the copolymer is predicted at 0.185 mole fraction in the monomer whereas only 0.648 is actually obtained.

A better fit of the available data (Table I) is obtained with eq. (2) where

$$r_1 = K^{aaa}/K^{aab} = 0.2$$

$$r_1' = K^{baa}/K^{bab} = 1.0$$

$$r_2 = K^{bb}/K^{ba} = 17$$

It is apparent from Table V that the reactivity of methyl methacrylate for an ethylene free radical is considerably reduced if the penultimate unit
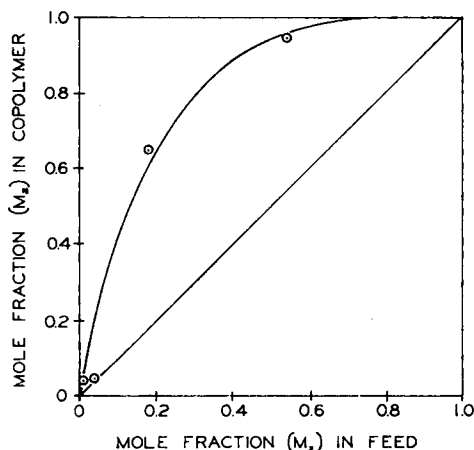

Fig. 2. Ethylene–methyl methacrylate copolymerization.

TABLE V

Ethylene–Methyl Methacrylate Copolymerization

Ratio of monomers A/B	Mole fraction of MMA in copolymer $[b/(a + b)]$		
	Points from expt. curve	$r_1 = K^{aa}/K^{ab} = 0.2,$ $r_2 = K^{bb}/K^{ba} = 17$	$K^{aaa}/K^{aab} = 0.2,$ $K^{baa}/K^{bab} = 1.0,$ $K^{bb}/K^{ba} = 17$
50	0.14	0.109	0.102
30	0.19	0.182	0.168
10	0.42	0.475	0.42
5	0.60	0.688	0.625
1	0.93	0.938	0.92

in the growing chain is methyl methacrylate. In the region where this effect is apparent, it is difficult to attribute the phenomenon to phase change effects. Much more feasible is the likelihood that polar and steric effects arising from penultimate methyl methacrylate units in the chain are much more readily transmitted across the terminal ethylene radical resulting in repulsion of adding methyl methacrylate monomer. Ethylene, as the smallest vinyl monomer and "chain unit component," exerts little shielding between penultimate methyl methacrylate unit and adding methacrylate monomer. On the other hand, it is doubtful that the addition of ethylene monomer to ethylene radical is influenced appreciably by whether the penultimate unit is ethylene or methyl methacrylate (except as this relates to "duality effects" involving ethylene monomer concentration). The consequence is that there is approximately 80% reduction in the reactivity of methyl methacrylate for an ethylene radical if the penultimate unit is methyl methacrylate rather than ethylene. This finding is of particular interest since methyl methacrylate does not contribute penultimate effects in most copolymerizations because of shielding effects of the other monomers involved, which, of course, have substituents not shared by ethylene.

Whether similar effects exist in the copolymerization of ethylene and methyl acrylate cannot be now ascertained because of the paucity of data in the intermediate region. It is probable that such effects are smaller (because of the greater configurational flexibility of methyl acrylate as a chain component).

It is interesting to examine the ternary system methyl methacrylate–methyl acrylate–ethylene and the three binary copolymer combinations which comprise it in the light of a new theory advanced by Ham.[5] This theory states that for systems of three monomers the following relationship holds:

$$P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba} = \mathcal{P}$$

where $\mathcal{P}$ is a constant. It follows that

$$r_{13}r_{21}r_{32} = r_{12}r_{31}r_{23} \tag{4}$$

Where the system is comprised of two conjugated monomers and one unconjugated monomer, experience has shown that $\mathcal{P} = 0.006$. Thus, to examine the system methyl methacrylate (M_1)–methyl acrylate (M_2)–ethylene (M_3) six reactivity ratios: r_{12}, r_{21}, r_{13}, r_{31}, r_{23}, and r_{32} are required to check the theory, or four ratios to predict the reactivity ratios for an untried combination. Thus, if r_{12}, r_{21}, r_{23}, and r_{32} are known, r_{13} and r_{31} can be predicted. For trial are chosen the values

$$r_{12} = 2.3 \text{ (Ref. 6)}$$

$$r_{23} = 11$$

$$r_{21} = 0.47 \text{ (Ref. 6)}$$

$$r_{32} = 0.2$$

From $P_{ab}P_{bc}P_{ca} = 0.006$ and $r_{12}r_{23}r_{31} = r_{13}r_{32}r_{21}$ it is determined that r_{13} (calcd.) $= 16.4$, r_{31}(calcd.) $= 0.061$; r_{13}(exptl.) $= 17$, r_{31}(exptl.) $= 0.2$.

The agreement with prediction for the copolymer system methyl methacrylate–ethylene is quite good, particularly when considered in the light of the "duality" of ethylene monomer. The high r_1r_2 product (3.4) creates difficulties in generalization. If one accepts r_1 and 0.1 and $r_2 = 17$ (r_1r_2 product $= 1.7$)

$$P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba}$$

$$0.0511 \qquad 0.00815$$

a result in good agreement with the prediction of equality and $\mathcal{P} = 0.006$.

The copolymerization of ethylene and diethyl fumarate also exhibited anomalous behavior. The best fit of the experimental data (Fig. 3)[7] was afforded by eq. (3).
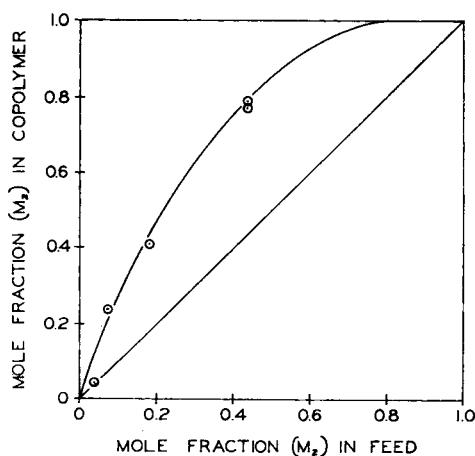

Fig. 3. Ethylene–diethyl fumarate copolymerization.

$$\frac{a}{b} = \frac{r_1''x\{[r_1x'(r_1\,x\,+\,1)/(r_1'\,x\,+\,1)]\,+\,1\}/(r_1''\,x\,+\,1)\,+\,1}{(r_2/x)\,+\,1} \qquad (3)$$

where

$$r_1 = K^{aaaa}/K^{aaab} = 0.25$$

$$r_1' = K^{baaa}/K^{baab} = 2.0$$

$$r_1'' = K^{baa}/K^{bab} = 2.0$$

$$r_2 = K^{bb}/K^{ba} = 10.0$$

The necessity for invoking the effects of remote chain units of diethyl fumarate is shown by a comparison with theoretical points for $r_1 = K^{aa}/K^{ab} = 0.25$ and $r_2 = 10$ (Table VI).

TABLE VI

	Mole fraction in copolymer				
Monomer ratio $x(A/B)$	Theoretical: K^{aa}/K^{ab} =0.25, K^{bb}/K^{ba} = 0.10	Theoretical: K^{aaa}/K^{aab} =0.25, K^{baa}/K^{bab} =1.0, K^{bb}/K^{ba} = 10	Theoretical: K^{aaa}/K^{aab} =0.25, K^{baa}/K^{bab} =2.0, K^{bb}/K^{ba} = 10	Theoretical: K^{aaaa}/K^{aaab} = 0.25, K^{baaa}/K^{baab} =2.0, K^{baa}/K^{bab} =2.0, K^{bb}/K^{ba} = 10.0	Experimental curve
10	0.364	0.323	0.32	0.28	0.26
5	0.57	0.51	0.498	0.444	0.43
1	0.90	0.87	0.86	0.833	0.86

Here again there is evidence that a penultimate (or penpenultimate) diethyl fumarate in a growing chain ending in an ethylene radical actively repels adding diethyl fumarate monomer.

Our conclusions about the copolymerization of ethylene and vinyl acetate are in agreement with those of Zutty and Burkhart[2] ($r_1 = 1.01$, $r_2 = 1$). Copolymerization of ethylene and diethyl maleate yielded $r_1 = 0.25$, $r_2 = 10$. Although our experiments were conducted at a relatively high temperature (150°C.) r_2 is unusually high for a diethyl maleate copolymerization.

It is believed that the above conclusions are valid and proceed directly from the available data. However, an adequate means of assessing the "duality" of ethylene monomer in copolymerization will be required before a full understanding of ethylene copolymerization is possible.

EXPERIMENTAL

Equipment

The equipment used in carrying out the copolymerizations is illustrated in Figure 4. It consisted primarily of a 250-ml. Magna Dash autoclave, an injection pot, pump, strain gage, pressure recorder, temperature recorder, vent assembly, earphones, and cold trap assembly. The term Magna Dash refers to the type of agitation obtained from a small dasher moving verti-
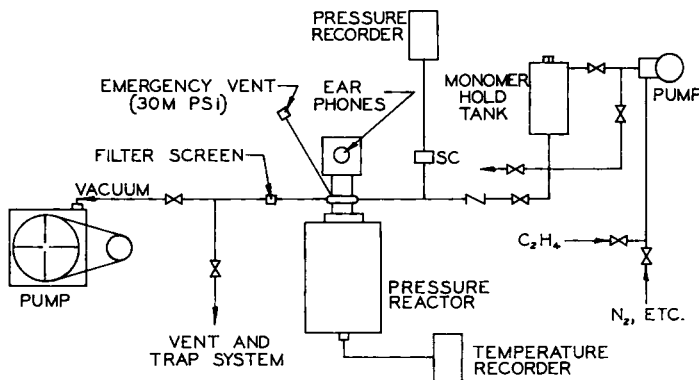

Figure 4.

cally up and down in the autoclave by a magnet cycling on and off exit the top section of the autoclave head. The autoclave internal temperature was recorded on a strip chart and regulated by steam pressure. A Baldwin-Lima 30,000 psi (max) strain cell was used. The pressure was recorded on an 8-hr. circular chart. The earphones were used to monitor the dasher action.

Procedure

The stainless steel autoclave was solvent-cleaned, air-dried, and placed within the heating element. It was then sealed, purged twice with 2,000 psig ethylene, and pressured to 4,000 psig. The desired internal temperature of 150°C. was obtained. The autoclave was then pressured to 8,000 psig. The valve on the autoclave side of the injection pot was closed and the comonomer and catalyst placed in the injection pot. The additives were then swept into the reaction vessel while raising pressure to the desired value, which in all instances was 12,000 psig. The external heating was kept constant and the reaction allowed to proceed for 30 min. During the 30 min. period the reaction vessel was isolated from the ethylene source and the pressure drop recorded.

The reaction was terminated by venting into a large cylinder. The gas from the cylinder was passed through a cold trap for isolation of entrained liquids. Following each reaction elaborate procedures were followed in cleaning the reactor and dasher mechanism.

The copolymerizations were carried out at a temperature (150°C.), pressure (12,000 psig), and catalyst concentration (2.7 × 10⁻⁴ moles of di-*tert*-butyl peroxide) which, for the homopolymerization of ethylene, resulted in a conversion of 6%. In the case of the copolymers the comonomers reached a higher conversion. The average total conversion, for example, of the methyl methacrylate runs, was about 7%. For methyl acrylate the average total conversion was about 13%.

References

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Résumé

On a étudié le comportement de l'éthylène lors de sa copolymérisation avec l'acrylate de méthyle, le méthacrylate de méthyle, l'acétate de vinyle, le fumarate de diéthyle, et le maléate de diéthyle et on donne les rapports de réactivité de ces différents systèmes. Pour tous ces systèmes étudiés sauf pour le système éthylène–acétate de vinyle, on constate d'importants écarts a l'équation classique de la copolymérisation et on les interprète sur la base d'effets pénultièmes et pen-pénultièmes non négligeables. L'accord entre les rapports de réactivité obtenus pour les systèmes éthylène–acrylate de méthyle et éthylène–méthacrylate de méthyle et les valeurs rapportées pour le système acrylate de méthyle–méthacrylate de méthyle est mis en évidence par l'application de la relation $P_{ab}P_{bc}P_{ca} = P_{ac}P_{cb}P_{ba}$.

Zusammenfassung

Das Verhalten von Äthylen bei der Copolymerisation mit Methylacrylat, Methylmethacrylat, Vinylacetat, Diäthylfumarat, und Diäthylmaleat wurde untersucht und Reaktivitätsverhältnisse für diese Systeme mitgeteilt. Es treten bei allen untersuchten Systemen mit Ausnahme von Äthylen–Vinylacetat charakteristische Abweichungen von der konventionellen Copolymerisationsgleichung auf, die auf wesentliche Einflüsse der vorletzten und vorvorletzten Kettenglieder Zurückgeführt werden. Die Konsistenz der im System Äthylen–Methylacrylat und Äthylen–Methylmethacrylat auftretenden Reaktivitätsverhältnisse mit Literaturwerten für Methylacrylat–Methylmethacrylat wird anhand der Beziehung $P_{ab}P_{bc}P_{ca}P = P_{ac}P_{cb}P_{ba}$ nachgewiesen.