Formation of a Cyclopropane Ester on a Polymer Support: Effect of the Macromolecular Backbone on the Stereoselectivity of Cyclization

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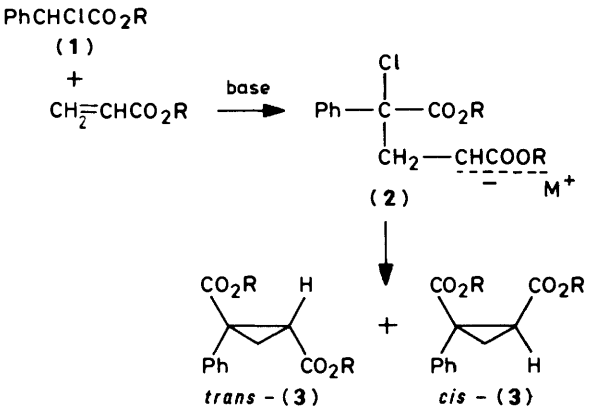
The stereoselectivity of cyclopropane ester formation was studied using reagents supported on linear or crosslinked polymers, and was compared with that obtained from low-molecular-weight compounds. The most important effects were noted with the crosslinked resin (2% DVB), in binary solvents or by lowering the temperature. The solvent effect was attributed to a specific solvation of the resin by one component of the mixture. The temperature influence would be the result of a restricted mobility of the macromolecular chain.

Polymers are widely used as supports of chemical reagents;[1-3] the steric and polar microenvironment of the bound reagents is expected to be different from the one encountered by the low-molecular-weight analogues (unbound substrates). This influence of the polymer backbone can lead to specific reaction paths in the heterogeneous medium.[4,5] We intended to see if the stereoselectivity of a reaction could be modified with such reagents. We chose a reaction which is sensitive to solvation effects (solvent polarity, cation–anion interactions) and to the steric bulk of substrates.[6,7] Furthermore, we previously studied this reaction in other heterogeneous media.[8] Thus, we examined the formation of the cyclopropane diesters (**3**) from acrylic and chloro(phenyl)acetic esters (**1**), supported on a linear or a crosslinked chloromethylated polystyrene. Results obtained with a linear polymer have already been reported.[9] In all cases, the stereoselectivity results were compared with those obtained, under the same conditions, with methyl esters.



Reaction Conditions.—The esters were bound on partially chloromethylated polymers which were either linear or crosslinked with 2% or 40% divinylbenzene (DVB). The linear polymer is obtained by a radical copolymerization of styrene and vinylbenzyl chloride (a *meta–para* mixture). The 2% DVB resin was obtained commercially (Merrifield resin). The others were prepared in order to have a well defined porosity: NC 13 is microporous, NC 28 and NC 27 are macroporous.† All the resins were only moderately loaded to enable accessibility of $-CH_2Cl$ groups during further chemical modification. The properties of the resins are given in Table 1.

† These resins were kindly donated by Professor Guyot, Lyon.

Table 1.

Resin	% DVB	Cl equiv. g^{-1}	Pore surface ($m^2\ g^{-1}$)
Linear		3.5×10^{-3}	
2% DVB	2	3.0×10^{-3}	
NC 13	40	2.6×10^{-3}	263 m^2/g
NC 28	40	2.23×10^{-3}	2.8 m^2/g
NC 27	10	2.21×10^{-3}	0.5 m^2/g

We first developed the reactions with the linear polymer. Thus, all the side-reactions leading to gel formation during functionalization can be avoided. Moreover, the different steps were followed by ^1H- or ^{13}C-n.m.r. spectroscopy. These methods are not well suited for the study of insoluble resins.

The chloro(phenyl) acetic and acrylic groups were fixed by reaction of the potassium acrylate or mandelate [hydroxy (phenyl)acetate] with the chloromethylated polymer in dimethylformamide (DMF). Even in this solvent the salts are only slightly soluble and not very reactive. Consequently, we added a catalytic amount of Bu_4NBr, a phase-transfer reagent, to increase both solubility and reactivity. The chlorination of the supported mandelic ester was effected by thionyl chloride in toluene. The ^{13}C n.m.r. chemical shifts were assigned by comparison with those of the corresponding vinyl monomers.

$$Ⓟ\text{–}CH_2Cl + CH_2{=}CHCO_2K \xrightarrow{Bu_4NBr} Ⓟ\text{–}CH_2OCOCH{=}CH_2$$

$$Ⓟ\text{–}CH_2Cl \xrightarrow[Bu_4NBr]{PhCH(OH)CO_2K} Ⓟ\text{–}CH_2OCOCH(OH)Ph \xrightarrow{SOCl_2} Ⓟ CH_2OCOCHClPh$$

The crosslinked polymers were modified by the same methods. The functionalization yields deduced from the elemental microanalyses were satisfactory only with the soluble polymer and the 2% DVB resin (Table 2). As previously reported in the literature[10] it was found that a high degree of crosslinking results in incomplete reaction. Contrary to all expectations, the accessibility of the CH_2Cl pendant groups is greatly reduced whatever the porosity. Consequently, these highly crosslinked polymers were no longer used, and the following data refer only to the linear polymer and the Merrifield resin.

The cyclization was performed in alkaline media, between one bound reagent and one low-molecular-weight compound (reactions A and B). In the case of the soluble polymer the two supported reagents were also condensed together (reaction C). In order to examine both solvent and cation effects, we chose different base–solvent combinations: Ph_3CLi–THF, $[(CH_3)_3Si]_2NK$–THF, and Ph_3CK in THF–DMSO mixtures (THF = tetrahydrofuran, DMSO = dimethyl sulphoxide).

Table 2. Degree of functionalization

Polymer	Ⓟ–$CH_2OCOCH{=}CH_2$	Ⓟ–$CH_2OCOCHClPh$
Linear	95	80
2% DVB	94	95
10% NC 27	14	29
40% NC 13	31	40
40% NC 28	38	32

In pure THF, another potassium base, $[(CH_3)_3Si]_2NK$, had to be employed, because the preparation of Ph_3CK requires one DMSO equivalent.[11] A gel formation was observed when the condensation step was performed with the linear polymer by reaction A. This implies polymerization of the attached acrylate molecules, due to a proximity effect. It is well known that bases such as Ph_2CHLi or Ph_2CHK are anionic polymerization initiators for analogous monomers.[12] Thus, we had to preform the ester anion before the acrylate addition. However, the ester enolates are very unstable at room temperature because of self-condensation, so the methyl chloro(phenyl)acetate is ionized at -60 °C[13] (reaction A). When the anion is supported, it is more isolated, and competing reactions occur less readily;[14] we therefore worked at -5 °C using reactions B and C.

increase of the *trans*-isomer proportion on going from Li^+ to K^+ as counter-cation (Table 3). The same variation [due to the strength of the cation–anion interaction in the intermediate (**2**)] is also observed with the unbound substrate moieties (hereafter called the small molecules) (see Figure 1).

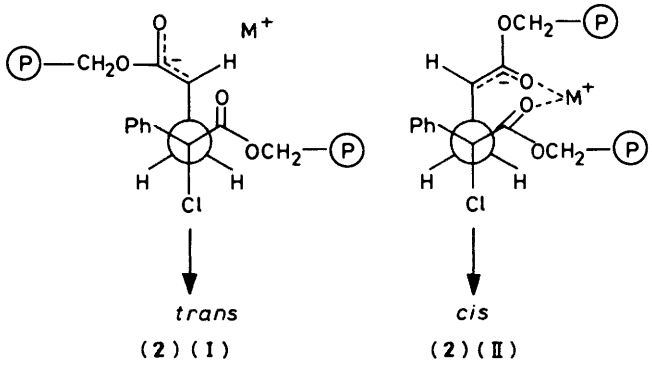
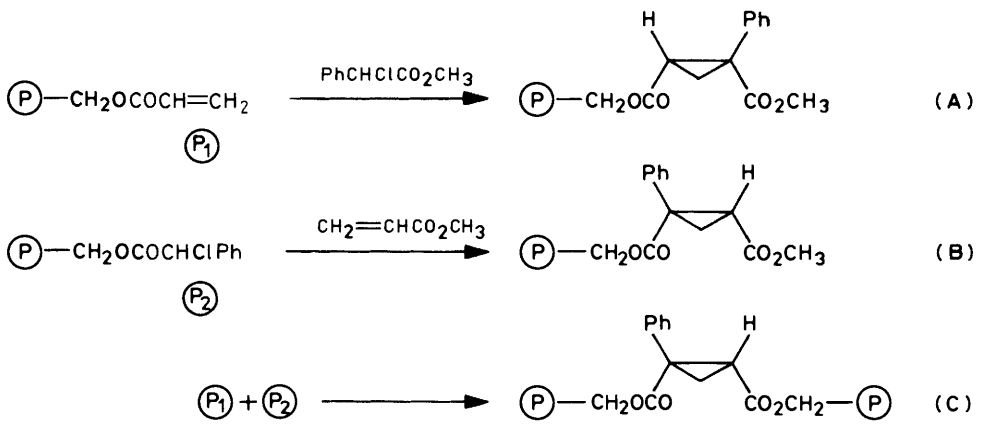
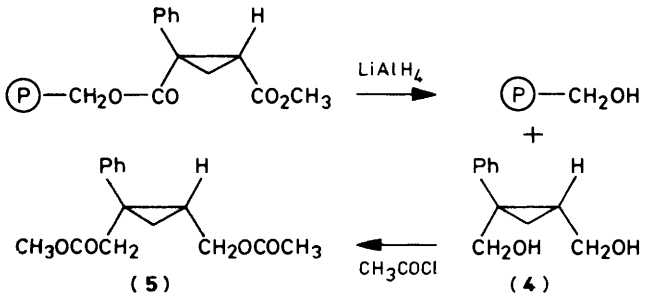


Figure 1.

Steric Effects.—The three modes of cyclization of the linear polymer give the same selectivity, under the same conditions of



Cleavage of the cyclopropane compounds from the macromolecular chain cannot be achieved by saponification with alcoholic KOH or by hydrolysis with a CH_3OH–HCl mixture. In both cases, only partial release of the product into solution occurs, together with polymer degradation. However, total cleavage was obtained by $LiAlH_4$ reduction in THF. The use of THF, a polymer-swelling solvent, may explain this satisfactory result. The *cis:trans* isomer ratio for the dihydroxymethylcyclopropane products (**4**) was determined by g.l.c. analysis after acetylation to give the diesters (**5**).



Results and Discussion

The stereoselectivity results obtained from the linear polymer in THF with Ph_3CLi or $[(CH_3)_3Si]_2NK$ as a base indicate an solvent and temperature (Tables 3 and 4). This means there is no particular steric hindrance caused by the polymer backbone. It is known that the stereoselectivity is determined during the cyclization step by the conformation of the intermediate (**2**).[8] It is reasonable to expect, therefore, that the *trans*-isomer should predominate in reaction C, due to the steric compression of the *cis*-alkoxycarbonyl groups in conformation (II) which leads to the *cis*-isomer.

Our result is similar to that of Leznoff: the regioselectivity of the Diels–Alder reaction performed with an acrylic ester and different dienophiles is not affected by the bonding of the acrylic group on a Merrifield resin.[15] The bulkiness of the polymer backbone does not impose greater steric constraints on

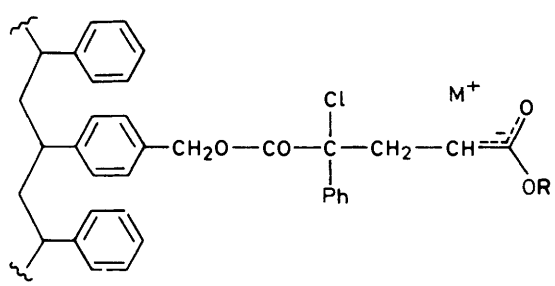


Figure 2.

the transition state than do the small molecules, probably because the active centre is too far from the polymer matrix and the adjacent phenyl groups (Figure 2).

Solvent Effects.—The experiments with the small molecules show the dependence of the stereoselectivity on solvent polarity: the more polar the medium, the greater the amount of *trans*-isomer formed.[8] From this point of view, a THF–DMSO mixture (90:10 v/v) is equivalent to a pure DMF solution. With the linear polymer, the solvent effects also exist, but the stereoselectivity differences are less important on going from THF to THF–DMSO (10%). In this last case, the *cis*:*trans* ratio reached 52:48 with the polymer and 40:60 with the small molecules. With the 2% DVB resin, a mixture of 3% or 10% DMSO in THF leads to the same *cis*:*trans* ratio (Table 3).

The greater formation of the *cis*-isomer with the polymer arises as a result of the less polar microenvironment in the surroundings of the bound reagent than in solution. It can be explained by the following factors:[16] (i) an apolar contribution of the polymer backbone or its aromatic substituents to the local microenvironment, and (ii) in binary solvents a preferential solvation of the polymer by one component. With the linear polymer, the first proposition is more satisfactory, since firstly, a THF–DMSO (90:10) mixture leads to the same results as DMF; accordingly, no preferential solvation of the resin can be proposed. Secondly, the differences with the small molecules are low, according to the weak polarity differences between the polymer and the bulk of the solution as demonstrated by physical measurements.[17] Furthermore, the chain influence decreases rapidly when the distance between the active centre and the chain increases.[16]

Unlike the soluble polymer it seems that, with the crosslinked resin, there is no interaction of DMSO with the solid phase, at least for low concentrations of DMSO in THF, and that THF exhibits a specific solvation of the resin. Thus, DMSO does not play any such role.

Temperature Effects.—With the polymer-bound esters, the stereoselectivity results depend on the temperature. The proportion of the *cis*-isomer increases as the temperature decreases (Table 3). A weak effect was noted with the linear polymer, and a stronger one with the Merrifield resin. Temperature dependence of stereoselectivity only occurs with condensations promoted by supported reagents: lowering the temperature from 20 to −60 °C did not change the *cis*:*trans* ratio with the low-molecular-weight compounds (Table 4). The proportions of the products are only affected by the solvent nature and the cation–anion interactions.

With the small molecules, we can suppose that the Curtin–Hammett principle applies.[18] Thus, the formation of the products is probably slower than the interconversion of the conformers of (**2**). This means that the rotation energy barrier is very low in comparison with the $\Delta G_{cis}^{\ddagger}$ and $\Delta G_{trans}^{\ddagger}$ activation energies of the cyclization process. The product composition is controlled by the differences in energies of the respective transition states (Figure 3). The absence of *cis*:*trans* ratio

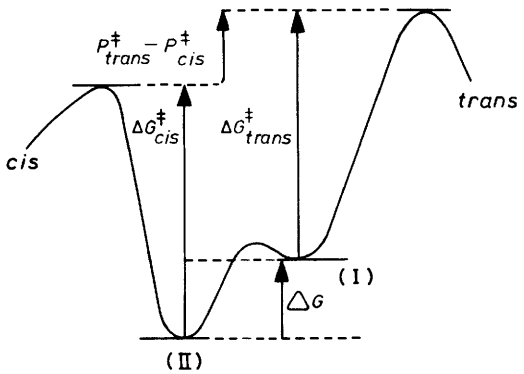


Figure 3. $\frac{d[cis]}{dt} / \frac{d[trans]}{dt} = {}_e(\Delta G_{trans}^{\ddagger} + \Delta G - \Delta G_{cis}^{\ddagger})/RT = {}_e(P_{trans}^{\ddagger} - P_{cis}^{\ddagger})/RT$

variation with temperature implies that the $P_{trans}^{\ddagger} - P_{cis}^{\ddagger}$ energy difference originates from an entropic variation and not from an enthalpic one. The solvent and the cation effects are brought about by differences in the structures of the anionic transition states leading to the *trans* and *cis* isomers.

With the polymer-supported reagents, it is likely that the equilibrium between the two intermediate conformations is slow relative to the cyclization steps. Consequently, the conformational energy barrier rises. Thus, the Curtin–Hammett principle cannot be applied. We must therefore take into account the populations of conformers (I) and (II) to determine the *cis*:*trans* product distribution (Figure 4).

Table 3. Stereoselectivity (*cis*/*trans*) with polymer-supported reagents

Conditions		Reaction[a]	With linear polymer	With 2% DVB resin
Ph_3CLi–THF	−60 °C	A	95/5	
	−5 °C	B	95/5	
$[(CH_3)_3Si]_2NK$–THF	−60 °C	A	81/19	88/12
	−5 °C	B	70/30	71/29
				69/31[c]
Ph_3CK–THF + DMSO (3%)	−60 °C	A	67/33	85/15
	−5 °C	B	52/48	75/25
	−5 °C	A	53/47	
	−5 °C	C	55/45	
Ph_3CK–THF + DMSO (10%)	−60 °C	A	55/45[b]	90/10
	−5 °C	B	48/52[b]	75/25
				71/29[c]
	−5 °C	C	49/51[b]	

[a] Reactions defined in the text. [b] The results in THF–DMSO (10%) are identical with those obtained in THF–DMF (40%). [c] Resin at 2.8×10^{-3} equiv. Cl g^{-1}; the other results refer to the reactions performed with the resin at 5×10^{-3} equiv. Cl g^{-1}.

Table 4. Stereoselectivity (*cis*/*trans*) with low-molecular-weight molecules

Temperature	Ph_3CLi–THF	Bu^{t}OK–Toluene	$[(CH_3)_3Si]_2NK$–THF	Ph_3CK–THF + DMSO (3%)	Ph_3CK–THF + DMSO (10%)*
20 °C	95/5	74/26	67/33	60/40	40/60
−5 °C				59/41	39/61
−60 °C				61/39	39/61

* See footnote (*b*), Table 3.

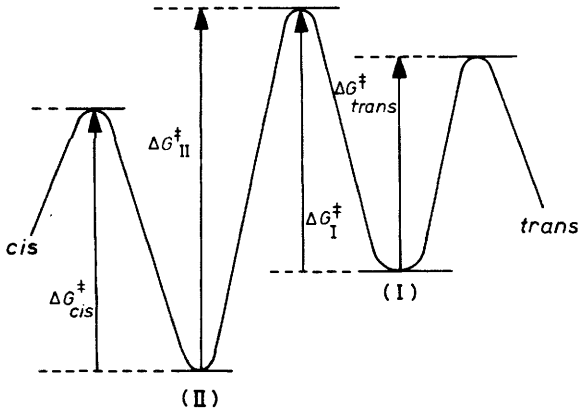
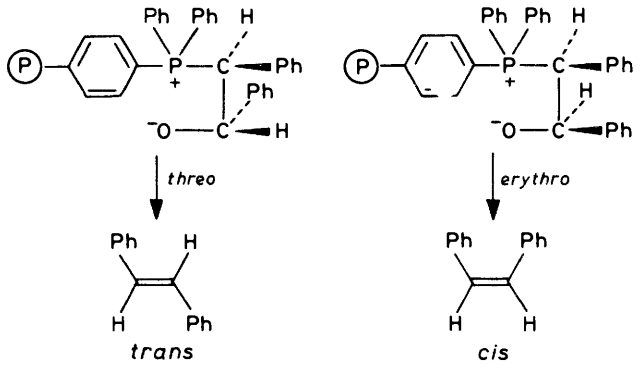


Figure 4.

It is well known that a lowering of the temperature leads to restricted chain mobility.[19] Reducing the flexibility of the chain may increase the potential energy barrier to conformational change of the pendant groups.[20] In our case, the most favourable conformation should be the one most ordered around the cation, *i.e.* (II) which leads to the *cis*-isomer.

Recently, Ford reported[21] that the selectivity of the Wittig reaction between benzaldehyde and a benzylphosphonium salt supported on a polymer is substantially affected by the degree of crosslinking. We can propose a similar explanation for our results. The increase of the DVB percentage in the resin reduces the macromolecular chain mobility,[19] so that the energy barrier between the two betaine conformers should rise, and the *threo*-isomer leading to the *trans*-stilbene product (**6**) should be favoured.



Conclusions.—This study on cyclopropane ester formation with polymer-supported reagents allows us to confirm some already known facts and to add some new contributions: the steric and polar microenvironment of a chloromethylated polystyrene is not different enough from the bulk of the solution to influence the selectivity of this reaction. Nevertheless, a specific influence of this solid phase can be observed by working (i) at low temperatures, when the chain mobility is reduced, and (ii) in binary solvents where a specific solvation of the polymer matrix can occur.

Experimental

Solvents were distilled as follows: toluene over Na, DMF and DMSO over CaH_2, under reduced pressure. THF was refluxed and distilled, firstly over $LiAlH_4$, and then over sodium benzophenone ketyl, under argon. I.r. spectra were recorded on a Perkin-Elmer model 577 spectrophotometer, using KBr discs for resins, or neat films between NaCl discs for the linear polymers. ^{13}C N.m.r. spectra were obtained using a Varian CFT 20 spectrometer at 20 MHz. The linear polymers were examined as solutions in deuteriochloroform. Elemental analyses were carried out by the Microanalysis Centre of the C.N.R.S., Lyon. G.l.c. analysis were performed on a Girdel model 75 chromatograph. All the polymers, described below, were dried under high vacuum for 12 h or overnight.

Preparation of Styrene–Vinylbenzyl Chloride Copolymer Ⓟ–CH_2Cl.—Styrene (Fluka) and vinylbenzyl chloride (Fluka) were each distilled under reduced pressure. The amount of each component was determined, so that the monomers represented 20 wt % of the toluene layer, and the initiator 1 wt % of the overall mixture of monomers. Styrene (59 ml, 0.51 mol) and vinylbenzyl chloride (43 ml, 0.3 mol) were introduced into a reactor filled with toluene (575 ml). Then azobis-isobutyronitrile (1 g) was added. This mixture was vigorously stirred at 70 °C under argon. After the solution had been cooled and concentrated the polymer was precipitated in methanol. Further purification was achieved by several dissolutions in methylene dichloride and precipitations in methanol. The polymer was then filtered off and dried *in vacuo* overnight; $\nu_{max.}$ (neat) 1 275 (C–Cl) and 1 600 and 1 500 cm^{-1} (aromatic ring vibrations) (Found: C, 81.0; H, 6.9; Cl, 12.1. Calc. for $(C_9H_9Cl)_x{\cdot}(C_8H_8)_y$: C, 81.08; H, 6.76; Cl, 12.16%). Cl equiv. $g^{-1} = 3.42 \times 10^{-3} - y/x = 1.34$. $\bar{M}_n$ (number average molecular weight) osmometric value 16 000 ± 400; δ_C 46.30 p.p.m. (CH_2Cl).

Functionalizations.—(a) *Preparation of potassium acrylate and mandelate.* The salts were obtained from the corresponding acids and alcoholic potassium hydroxide. They were collected by precipitation of the alcoholic salt solution in benzene, then filtered and dried *in vacuo*.

(b) *Preparation of polymer-bound acrylate* Ⓟ–$CH_2OCOCH{=}CH_2$. The linear chloromethylated polystyrene (10 g, 34 mmol) was dissolved in DMF (200 ml). Bu_4NBr (0.1 equiv.) and potassium acrylate (1.2 equiv.) were added. The mixture was stirred at 60 °C for 24 h. After being cooled, the solution was filtered to remove the insoluble salts, and the filtrate was poured into water. The polymer was recovered by filtration and purified by dissolution in THF and precipitation in methanol. The crosslinked polymer was allowed to swell in DMF for 2 or 3 h before addition of the salt. The reaction was performed under the same conditions as described above. Finally, the solution was filtered and the resin was washed in a fritted funnel with the following solvents: twice with water and THF, once each with methanol, CH_2Cl_2, and pentane. The resin showed the following properties. $\bar{M}_n$ osmometric value 25 250 ± 250; $\nu_{max.}$ 1 725 (C=O), 1 640 (CH=CH_2 conj.), and 1 075 cm^{-1} (C–O); δ_C 66.20 (CH_2O), 115 (COCH=CH_2), 130.91 (COCH=CH_2), and 166 p.p.m. (C=O).

(c) *Preparation of polymer-bound chloro(phenyl)acetate. Polymer-bound mandelate* Ⓟ–$CH_2OCOCH(OH)Ph$. We used a procedure similar to that described for the binding of the acrylic acid group. Since the linear polymer swelled in methanol, it was purified by several dissolutions in THF and precipitations in water. The last precipitation was effected in pentane. The resin showed $\nu_{max.}$ 3 400 (O–H), 1 735 (C=O), and 1 080 and 1 100 cm^{-1} (C–OH); δ_C 67.52 (CH_2O), 72.98 (CHOH), and 173.47 p.p.m. (C=O).

Chlorination Ⓟ–$CH_2OCOCHClPh$. Thionyl chloride (3.2 ml, 2 equiv.) was added to a solution or a suspension of Ⓟ–$CH_2OCOCH(OH)Ph$ (9 g, *ca.* 2.5×10^{-3} equiv. OH g^{-1}). The mixture was heated and magnetically stirred at 60 °C for 12 h. In the case of the linear polymer, the toluene was partially evaporated, and the polymer was recovered by precipitation in methanol and purified by dissolutions in THF, followed by successive precipitations in saturated aqueous

$NaHCO_3$, in distilled water, and finally in pentane. In the case of the resin, the product was separated from the DMF solution and washed in turn with the following solvents: methanol, saturated aqueous $NaHCO_3$, distilled water, THF, MeOH, THF, and pentane. The chlorinated resin had $\bar{M}_n$ osmometric value 17 250; $\nu_{max.}$ 1 750 (C=O) and 1 160 cm^{-1} (C–Cl); δ_C 59.04 ($CHCl$), 67.94 (CH_2O), and 168.53 p.p.m. (C=O).

(d) *Microanalysis results. From the linear polymer.* Ⓟ–$CH_2OCOCH{=}CH_2$: (100% functionalized) [Found: C, 83.0; H, 6.95; Cl, 0.0. Calc. for $(C_8H_8)_{1.34}(C_{12}H_{12}O_2)_1$: C, 83.28; H, 6.94%]. Ⓟ–$CH_2OCOCHClPh$: [Found: C, 78.1; H, 6.3; Cl, 9.05. Calc. for $(C_8H_8)_{1.34}(C_{17}H_{15}ClO_2)_1$: C, 78.11; H, 6.04; Cl, 8.34%]. The functionalization was not quantitative. The composition of the polymer would be $(C_9H_9Cl)_{1-\alpha}{\cdot}(C_{17}H_{15}ClO_2)_\alpha{\cdot}(C_8H_8)_{y/x}$. The α value could be obtained from the ratio of O (remainder) and Cl percentages in the found analysis: $32\alpha/35.5 = 6.51/9.95$, $\alpha = 0.8$. For $\alpha = 0.8$ the theoretical analysis was deduced: C, 78.54; H, 6.14; Cl, 8.90 (O, 6.42)%.

From the Merrifield resin with 4.98×10^{-3} equiv. Cl g^{-1} and 2% DVB $[(C_9H_9Cl)_x{\cdot}(C_8H_8)_y]_2{\cdot}(C_{10}H_{10})_z$. From the loading of chlorine and the weight percentage of DVB, the composition of the resin was determined as $x = 16.2$, $y = 6.87$, and $z = 1$.

Ⓟ–$CH_2OCOCH{=}CH_2$ (Found: C, 78.8; H, 6.5; Cl, 1.0%). The composition of the polymer should be $[(C_9H_9Cl)_{x-\alpha}{\cdot}(C_{12}H_{12}O_2)_\alpha\ (C_8H_8)_y]_2{\cdot}(C_{10}H_{10})_z$; the α value was deduced from the found Cl and O (remainder) percentages: 35.5 $(x - \alpha)/32\alpha = \%Cl/\%O = 0.97/13.43$. The degree of functionalization was obtained as $\alpha/x = 94\%$. For this α/x value, the calc. analysis is: C, 79.59; H, 6.63; Cl, 0.94 (O, 12.83)%.

Ⓟ–$CH_2OCOCHClPh$ (Found: C, 74.6; H, 5.65, Cl, 10.5%); hence for $[(C_9H_9Cl)_{x-\alpha}{\cdot}(C_{17}H_{15}ClO_2)_\alpha{\cdot}(C_8H_8)_y]_2{\cdot}(C_{10}H_{10})_z$, $32\alpha/35.5x = \%O/\%Cl = 9.23/10.54$. The degree of functionalization was $\alpha/x = 97\%$, a value for which the calculated analysis was: C, 74.27; H, 5.60; Cl, 10.73 (O, 9.39)%.

From the macroporous and microporous resins. We give the composition of the starting resin, then for the functionalized polymers, the O (remainder) and Cl percentages found in the analysis, and the degree of functionalization α/x.

NC13 $x = 0.35$, $y = 0.42$, $z = 1$.

NC27 $x = 1.44$, $y = 3.51$, $z = 1$.

NC28 $x = 0.36$, $y = 0.41$, $z = 1$.

Ⓟ–$CH_2OCOCH{=}CH_2$·NC13: (O, 2.60) Cl, 6.3%; α/x 31.5%. NC28: (O, 3.17) Cl, 4.9%; α/x 38.5%. NC27: (O, 1.16) Cl, 7.6%; α/x 14%.

Ⓟ–$CH_2OCOCHClPh$·NC28: (O, 2.85) Cl, 9.9%; α/x 32%. NC27: (O, 2.06) Cl, 7.8%; α/x 29%.

Ⓟ–$CH_2O(C{=}O)CH(OH)Ph$·NC13: (O, 4.00) Cl, 4.6%; α/x 40%.

Condensation Reactions.—(a) *Preparation of the bases.* The bases were obtained according to procedures previously reported in the literature: Ph_3CLi,[22] Ph_3CK,[11] and $[(CH_3)_3Si]_2NK$.[23] Their accurate concentrations were known by back-titration.

(b) *Cyclization process.* All these reactions were performed under argon with freshly distilled solvents. The concentrations of the reagents were 0.15M for reactions A and B and 0.075M for reaction C. The apparatus was fitted out with a mechanical overhead stirrer for reactions A and C, and with a magnetic stirrer for reaction B.

Reaction A. A solution of $PhCHClCO_2CH_3$ (7.5 mmol) in solvent (5 ml) was added dropwise to a solution of base (1.1 equiv.) in solvent (v ml) cooled at −60 °C. The mixture was stirred for 15 min, then a solution or a suspension of the polymer in solvent [(45 − v) ml] was added through a dropping funnel for the linear polymer, or through a syringe *via* a rubber septum for the resin. The mixture was stirred at −60 °C for 4 h, and was then allowed to warm up to room temperature. The solution of the linear polymer was poured into water (1 l). The polymer was recovered, and purified by dissolution in THF and precipitation in methanol. The crosslinked polymer was filtered off and successively washed with water, THF, MeOH, THF, and pentane.

Reaction B. Base (1.1 equiv.) in solvent (v ml) were added to Ⓟ–$CH_2OCOCHClPh$ (7.5 mmol) dissolved or swelled in solvent [(45 − v ml] stirred at −5 °C. 15 Min later, a solution of methylacrylate (1 equiv.) in solvent (5 ml) was added dropwise. After being stirred for 4 h the mixture was treated as previously described.

Reaction C. The condensation of the two polymers together led to formation of a gel, the degree of swelling of which was high. Hence, a greater volume of solution was needed. The overall volume had to be increased to 100 ml. The mixture was poured into water (1 l) and easily filtered. The gel was swelled in THF and poured into methanol (1 l).

(c) *Reduction of the polymer-bound cyclopropane compounds.* A solution of $LiAlH_4$ (8 H^- equiv.) in THF was added, through a syringe *via* a rubber septum, to a cooled solution of the polymer dissolved or swelled in THF (25 ml) (50 ml for the gel). (Twice the theoretical amount of $LiAlH_4$ was used because the formation of an alkoxyaluminohydride bridge led to gel formation, and all the 4 H^- contained in one molecule might not be reactive.) After being stirred for 3 h at room temperature the mixture was hydrolysed with a 50:50 (v/v) mixture of 6M-HCl and THF. The mixture was stirred for several hours. Then, the solutions of reactions A, B, and C performed with the *linear* polymer became clear. They were poured in water. The aqueous layer was extracted three times with diethyl ether, and the recovered polymer was also washed with diethyl ether. The combined ethereal layers were dried (anhydrous $MgSO_4$) and evaporated. The residue contained the *trans* and *cis* dihydroxymethylcyclopropane (**4**). The resins were filtered off and washed in turn with water and diethyl ether; the filtrates were worked up as described above. The i.r. spectra of the recovered polymers showed that there was no more C=O stretch at 1 750 cm^{-1}, but a new absorption band at 3 400 cm^{-1} was noted.

(d) *Acylation of the dihydroxymethylcyclopropane mixture.* The acylation was carried out with acetyl chloride in toluene. The mixture was refluxed and stirred for 2 h. After being cooled, the mixture was poured into saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The dried extract was concentrated by partial evaporation of the solvent. The residue containing the diesters (**5**) was subjected to g.l.c. analysis on an OV 225 column, 2 m long, at 220 °C. N_2 was used as gas carrier (pressure 1.9 kg cm^{-2}). The retention times were: *trans*-isomer, 26 min; *cis*-isomer, 28 min. Each *cis* : *trans* ratio quoted in Tables 3 and 4 was the average from two or three independent experiments.

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Received 7th November 1983; *Paper* 3/1979