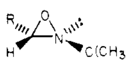
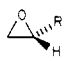
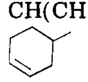
Table II. LCICD of Oxaziridines and Epoxides in MBBA


2


3

compd	R	induced CD,[a] 2% in MBBA
2a	CH_3	–
2b	$CH(CH_3)_2$	–
2c		–
2d	$PhCH_2$	–
2e	4-BrPh	–
2f	1-naphthyl	–
3a	Ph	+
3b	*n*-octyl	–
3c	C_2H_5	–
3d	CH_3	–

[a] From MBBA chromophore at 410-430 nm.

were of the same absolute configuration (i.e., 2*S*,3*S*) as (–)-**2a-d**. This conclusion was supported by NMR–chiral solvating agent studies.[9]

Epoxides. The LCICD data for several (*R*)-(+)-epoxides[10] appears in Table II. Although too little data are at hand to warrant discussion, it is apparent that **3a**, styrene oxide, behaves differently than the alkyl-substituted epoxides **3b–d**.

Conclusion. Evidence is offered to support the contention that LCICD is systematic and that it may be possible to use the technique as a means of reliably assigning absolute configurations. In any event, the sensitivity of the technique makes it valuable even now as a chirality amplifier. For example, various chiral insect pheromones have been isolated in amounts too small to allow chiroptic measurements. In such instances, the absolute configuration of the natural pheromone might be determined through comparison of its LCICD with that of suitable configurationally established model compounds. These model compounds might be synthetic samples of the pheromone enantiomers.

Experimental Section

Circular dichroism spectra were obtained by using a Jasco J-40 spectrometer, and optical rotations were obtained by using a Zeiss visual polarimeter and a 1-dm tube.

Chiral Alcohols 1a–q. These alcohols were synthesized and resolved by procedures previously described.[11-14] The characterization and absolute configuration determination for the following alcohols have previously been reported: **1a** and **1b**;[14] **1o** and **1p**;[11] **1c–j**;[13] **1g** and **1k**.[14] **1m** and **1n** were provided by Mr. K. Simmons, University of Illinois. Their configurations were determined as previously described.[8a]

Oxaziridines 2a–f. Oxaziridines were synthesized enantiomerically enriched (15–60%) by monoperoxycamphoric acid oxidation of the corresponding imines, as previously described.[9]

Epoxides 3a–d. These epoxides were prepared and resolved as previously described.[10]

Examination of LCICD in MBBA. Solutions of chiral substrate were made by adding the substrate (~2% by weight) to MBBA and heating the mixture above the liquid-crystal–liquid transition temperature (~40 °C). One drop of this solution was placed between two glass slides with 24-μm Mylar spacers. The mounted plates were placed in the CD instrument and allowed to cool. As the cholesteric mesophase formed, optical activity could be detected in the region of 390–410 nm. The CD spectrum was scanned from 700 to 200 nm. Although no pitch bands were ever observed, an intense CD band associated with the conjugated imino group of MBBA was always apparent at 390–410 nm. The above procedure was repeated a total of 3 to 5 times to eliminate the possibility that the observed CD band was a result of mechanical twisting of the plates. The importance of this precaution cannot be overstressed. We originally misassigned the LCICD sign for *S*-(+)-**1a** (**1a** gives a weaker than usual LCICD) and noted the error only after Professor Gottarelli informed us of his differing assignment for **1a**. Runs without chiral dopant afforded only weak random CD activity of mechanical origin.

Acknowledgment. This work was partially supported by grants from the National Science Foundation and the National Institutes for Health.

Registry No. (*S*)-(+)-**1a**, 340-06-7; (*S*)-(+)-**1b**, 33758-06-4; (*S*)-(+)-**1c**, 60646-30-2; (*S*)-(+)-**1d**, 63017-54-9; (*S*)-(+)-**1e**, 59153-46-7; (*S*)-(+)-**1f**, 73048-43-8; (*S*)-(+)-**1g**, 73048-44-9; (*S*)-(+)-**1h**, 73048-45-0; (*R*)-(–)-**1i**, 73048-46-1; (*S*)-(+)-**1j**, 59153-45-6; (*S*)-(+)-**1k**, 53432-38-5; (*S*)-(–)-**1m**, 73048-47-2; (*S*)-(–)-**1n**, 73048-48-3; (*S*)-(+)-**1o**, 73048-49-4; (*R*)-(–)-**1p**, 73048-50-7; (*R*)-(–)-**1q**, 73048-51-8; **2a**, 62107-41-9; **2b**, 67504-37-4; **2c**, 67425-89-2; **2d**, 67425-90-5; **2e**, 62058-74-6; **2f**, 67425-91-6; **3a**, 20780-53-4; **3b**, 67210-36-0; **3c**, 3760-95-0; **3d**, 15448-47-2.

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[10] W. H. Pirkle and P. L. Rinaldi, *J. Org. Chem.*, **43**, 3803 (1978).

[11] T. G. Burlingame, Ph.D. Thesis, University of Illinois, Urbana, IL, 1970.

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Memory of Synthesized Vinyl Polymers for Their Origins[1]

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We report herein studies on the memory of a highly cross-linked styrene–divinylbenzene copolymer for its origins. Specific experiments are described which indicate that vinyl polymers synthesized from diastereoisomers of truxinic and truxillic acid are able to recognize the stereoisomer appended during their synthesis, in subsequent chemical transformations. Specific characteristics of polymer cross-link density and other factors as related to the specificity of recognition are outlined.

Nature's "trial and error" chemistry over an enormous length of time, conducted in tremendous numbers, has led to ingenious and refined systems. Efficient catalysts allow reactions to proceed under ordinary conditions, whereas

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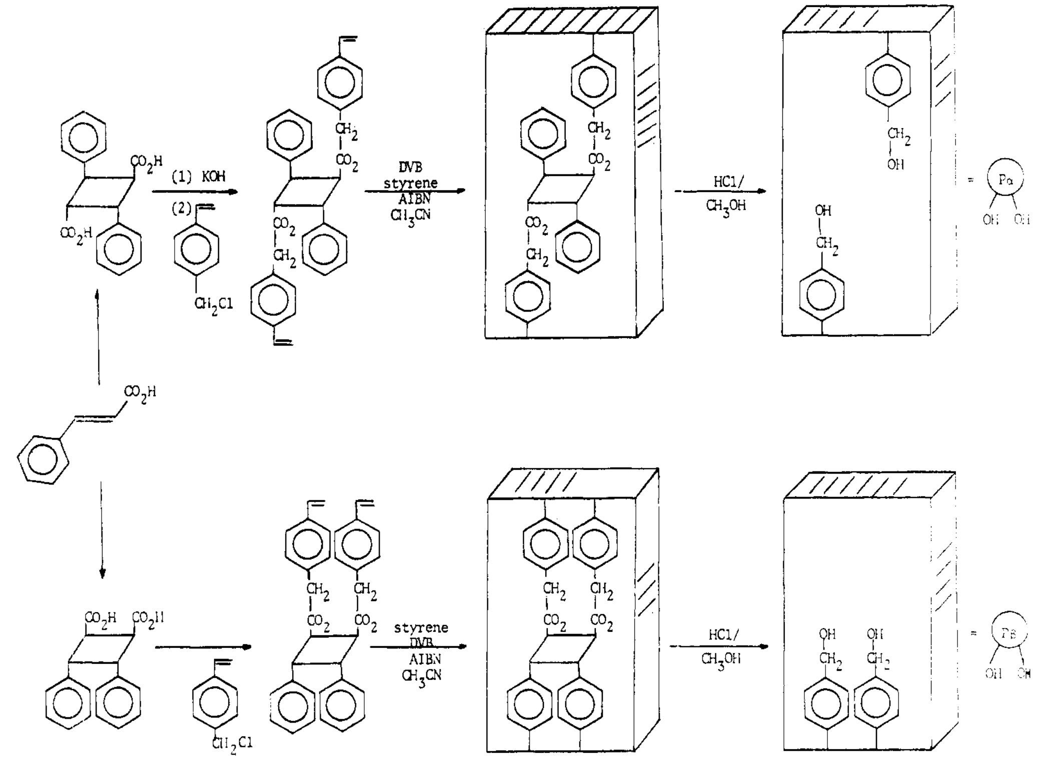
Scheme I



noncatalyzed reactions require, sometimes, extremely complex approaches or may not work at all. It has always been man's dream to simulate nature's chemistry. The synthesis of organic compounds which simulate enzyme action has become an important area in synthetic organic chemistry.[2]

Enzyme activity is based on the specificity of binding of a substrate at the surface of the enzyme through a stereospecific arrangement of active groups. The introduction of organic functionalities in a stereospecific manner which later may be able to select one particular substrate is one way of simulating enzyme activity.

The principle on which our work is based and reported herein is that of Dickey,[3] who demonstrated that silica gel, prepared from sodium silicate and acetic acid in the presence of methyl orange, had a specific affinity for methyl orange in the presence of the ethyl, *n*-propyl, and *n*-butyl isomers. More recent work, first by Wulff[4] and later by Shea[5] has shown that a macromolecule may develop a molecular pattern recognition during its construction which is based on the monomer from which the macromolecule was constructed—even though the specific molecules of construction no longer remain in the polymer.

Contemporary interest in the use of synthesized polymers in chemical processes has led to many important new developments in solid-phase synthesis.[6] Most of the successful applications have used already synthesized polymers as handles in the preparation or separation of organic compounds.[7] As part of a program designed to take advantage of the properties of polymers in organic processes,[8] we have been investigating the synthesis of polymeric materials which maintain a recognizable macrostructure throughout subsequent chemical reactions.

In this paper we describe the synthesis of different copolymers and their subsequent use in the resolution of an enantiomeric mixture and in the separation of several diastereoisomers. This important phenomenon is based on *the selective memory of the synthesized polymer for its origins.*

Results and Discussion

In a previous paper,[1] we reported on the use of a vinyl polymer in the partial resolution of a racemic mixture of (*tert*-butoxycarbonyl)proline (*t*-BOCpro). Specifically *t*-BOC-L-pro was converted to a polymerizable derivative—(*tert*-butoxycarbonyl)-L-proline vinylbenzyl ester. This monomer was then copolymerized with styrene and divinylbenzene via suspension polymerization[9] (molar

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[1] See also: Damen, J.; Neckers, D. C., submitted for publication in *Tetrahedron Lett.*

[2] (a) Griffiths, D. W.; Bender, M. L. *Adv. Catal.* **1973**, *23*, 209. (b) Overberger, C. G.; Sannen, K. N. *Angew. Chem.* **1974**, *86*, 139. (c) Kunitake, T.; Okahato, Y. *Fortschr. Hochpolym.-Forsch.* **1976**, *20*, 159. (d) Shimidzu, T. *Ibid.* **1977**, *23*, 56. (e) Tsuchida, E.; Miskide, H. *Ibid.* **1977**, *24*, 1.

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[9] The reaction mixture composition was 50 mL of deaereated water, 10 mg of lauryl sulfate, 150 mg of sodium polyacrylate, 500 mg of sodium sulfate, 150 mg of stearic acid, 70 mg of benzoyl peroxide, 100 mg of gelatin, 4.12 g of (*tert*-butoxycarbonyl)-L-proline vinylbenzyl ester, 8.92 g of divinylbenzene, and 4.55 g of styrene. It was heated at 60 °F under N_2 with stirring for 5 h. The obtained polymer was filtered and washed in a Soxhlet extractor overnight with methanol.

Table I. Copolymers of Bis(vinylbenzyl) α-Truxillate 3 and Bis(vinylbenzyl) β-Truxinate 4 with Styrene and Divinylbenzene

polymers	composn of polymer mixture, mol % 3	4	sty[a]	DVB[b]	F_M[c]	solvent regain, mL/g of polymer toluene	methanol	cyclohexane
[Pα_1]	4.8		69.6	25.6				
[Pα_2]	3.6		38.3	58.0				
[Pα_3]	5.0		29.8	65.2				
[Pβ_1]		5.0	95.0		0.48	2.07	0.12	0.09
[Pβ_2]		5.0	93.2	1.8	0.49	1.64	0.00	0.00
[Pβ_3]		4.9	90.3	4.8	0.49	2.10	0.04	0.07
[Pβ_4]		6.0	82.1	11.9	0.49	1.30	0.12	0.11
[Pβ_5]		5.6	63.1	31.3	0.49	1.24	1.10	1.12
[Pβ_6]		5.0	30.0	65.0				
[Pβ_7]		4.9		95.1	0.51	0.99	0.93	0.88

[a] Styrene. [b] Divinylbenzene. [c] F_M = (weight of monomer mixture)/(total weight of monomer mixture plus solvent).

composition 10:35:55). Cleavage of the *t*-BOC-L-pro from the resin with $\mathrm{HBr/CF_3CO_2H}$[10] produced holes with active functionalities containing a Br leaving group, which in a subsequent nucleophilic displacement was able to bind specifically *t*-BOC-L-pro from a mixture of D- and L-*t*-BOCpro. More specifically, the obtained polymer was treated with the Cs salt of a racemic mixture of *t*-BOCpro and subsequently hydrolyzed with $\mathrm{HBr/CF_3CO_2H}$. The hydrolysate was richer in L form (L/D ratio of 1.025)[11] while the excess Cs salt showed an enrichment in D form. The enantiomeric excess indicated that 1.2% of the holes were able to distinguish between D- and L-*t*-BOCpro.

One must visualize a highly cross-linked polymer as a tridimensional network of long chains whose preference for one particular substrate over another is caused by the steric interaction of the polymer chain with the substrate. The more the special structure of the substrate differs from the model compound structure, the higher the energy barrier and hence the slower the chemical reaction with the polymer. The energy of interaction of polymer with substrate is, therefore, expected to be smallest for the originally present model compound, and a small, mobile substrate such as a chiral amino acid is expected to give a minimal effect. A polymer constructed from a molecule containing big bulky phenyl groups would be expected to be more selective.

We chose, therefore, the diastereoisomers α-truxillic acid and β-truxinic acid as model compounds for subsequent use in photochemical reactions.[12]

trans-Cinnamic acid gives, on irradiation in the solid state, α-truxillic acid 1 and β-truxinic acid 2, depending on the crystal structure of the starting cinnamic acid[13] (Scheme I). Acids 1 and 2 when converted to their dipotassium salts and treated with an excess of vinylbenzyl chloride in the presence of 18-crown-6 ether[14] formed the bis(vinylbenzyl) derivatives of α-truxillic and β-truxinic acids, 3 and 4. These monomers, 3 and 4, were copolymerized with styrene and divinylbenzene[15] via radical polymerization with AIBN as initiator in the presence of an inert solvent to give the α and β polymers, respectively (Table I). Polymerization was performed in sealed tubes, previously degassed by five freeze–thaw cycles. After polymerization, the tubes were broken and the obtained white polymers ground up mechanically with mortar and pestle. After washing in a Soxhlet extractor with toluene and methanol and drying in a vacuum oven at 50 °C, a white crushed polymer was obtained. The IR spectra of these polymers showed the superposition of the ester function (ν 1730 cm^{-1}) over the spectrum of a styrene–divinylbenzene copolymer.

Since all monomers used were styrene derivatives, their relative reactivities (r) must be approximately 1,[16] and this results in a random distribution of the different monomers in our polymers.[17]

In order to obtain highly cross-linked polymers with the maximum accessibility to as many reaction centers as possible, we prepared macroreticular polymers by carrying out the polymerization in the presence of an inert solvent (acetonitrile). A tridimensional network of polymer chains interspaced by the solvent is formed, and after removal of the acetonitrile the network collapses, leaving some macropores behind in the macromolecule.[18] The uptake of nonswelling solvents is a measure of the number and volume of the macropores. The solvent-regain experiments (Table I) show that the polymers [Pβ_5] and [Pβ_7] show the same affinity for good swelling solvents (toluene) and nonswelling solvents (methanol and cyclohexane). In these highly cross-linked polymers the swelling is negligible, and the pore volume alone determines the solvent uptake. With lower degrees of cross-linking, we see a higher toluene uptake than nonswelling solvent uptake.

Macroporosity for styrene–divinylbenzene copolymers is defined by Millar[19] as copolymers in which cyclohexane uptake is higher than 0.1 mL/g of dry polymer. From Table I we see that macroporosity disappears with lower degrees of cross-linking. For copolymers with less than 10% cross-linking there is virtually no more solvent regained. It should be noted that conventionally prepared styrene–divinylbenzene copolymers show little or no affinity for nonsolvents.[19]

Acidic hydrolysis in methanol of the original truxinate and truxillate copolymers (Scheme I) was repeated several times until no more model residue was hydrolyzed, leaving two benzyl alcohol groups behind in the polymer for each molecule of truxillic or truxinic acid liberated.[5] Under

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[10] Reaction with hydrobromic acid in trifluoroacetic acid[5] at room temperature gave us the mild hydrolysis conditions by which we might conserve as much as possible the shape of the macromolecular hole, and it produced a good leaving group (bromide) on the polymer for the rebinding of the amino acid.

[11] The composition of this mixture was measured from the optical rotation in glacial acetic acid.

[12] Polymers based on truxinic and truxillic acids are used to guide the photochemical reaction of *trans*-cinnamic acid.

[13] Cohen, M. D.; Schmidt, G. M. J.; Sonntag, F. I. *J. Chem. Soc.* **1964**, 2000.

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[15] Technical divinylbenzene was used. This monomer contained, besides *m*- and *p*-divinylbenzene, some monovinyl derivatives.

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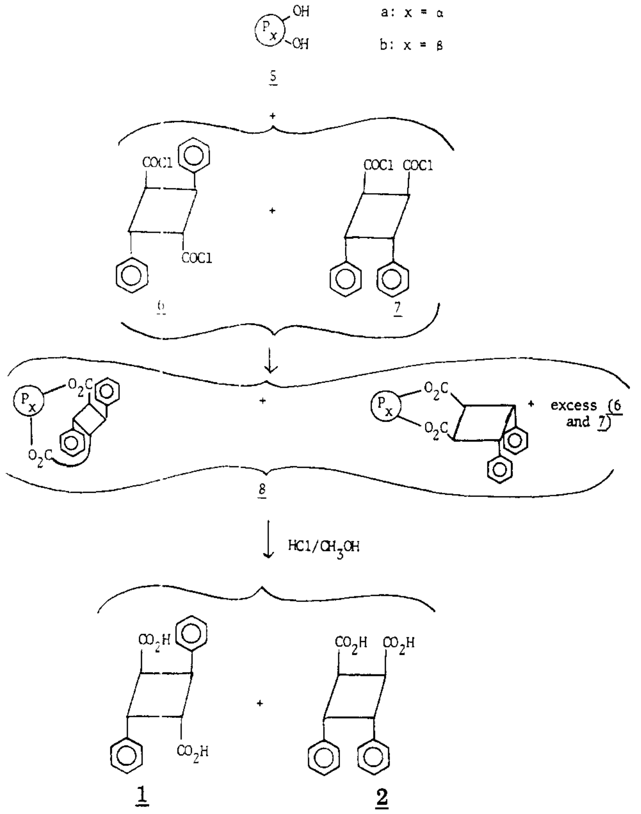
Scheme II



these circumstances a maximum of 70% of the template assemblies would be liberated (Table II).

The remaining functionalities, surrounded by long polymer chains, were then treated with a mixture of α-truxillic acid chloride **6** and β-truxinic acid chloride **7** of known composition (Scheme II). Were there no important structural changes during the hydrolysis step and if the macromolecular structure remained rigid enough to prevent important secondary molecular motion, we would expect a lower energy barrier for the reaction of the polymer with the compound originally present than for the reaction of the polymer with a diastereoisomer of the model compound, due to steric hindrance exhibited by the macromolecular chains. In this case the reaction with the model compound should be faster and hence more model compound built into the polymer. The excess acid chloride, on the other hand, is expected to be richer in the diastereoisomer of the model compound.

The use of [Pβ_5] in the separation of the diastereoisomers α-truxillic acid and β-truxinic acid is given here as a typical example (see Table II). Thus, 0.8821 g of hydrolyzed [Pβ_5], containing 152 μequiv of holes/g of dry polymer, was treated with a mixture of 103 μmol of α-truxillic acid chloride (**6**) and 105 μmol of β-truxinic acid chloride (**7**) in ether. After a 24-h reaction at room temperature under a dry nitrogen atmosphere, the excess acid chloride was extracted by washing the polymer with warm ether. Acid chloride (30.1 mg, 0.90 mmol) was recovered. The composition of the excess acid chloride, determined as the methyl ester by GC on a 3 ft × $^1/_8$ in. column filled with 20% Carbowax 20-M on Chromosorb P, was 54 μmol (59.7%) of α-truxillic and 36 μmol (40.2%) of β-truxinic. From the difference between the quantity of α-truxillic and β-truxinic acid chloride starting mixture and that obtained after the reaction, the amount of acid chloride built into the polymer could be calculated. A specific adsorption of β-truxinic acid chloride in the presence of α-truxillic acid chloride because of complex formation between it and the

Table II. Polymer Composition and the Memory Effect

polymer	% hydrolysis	mequiv of holes/g of polymer	wt of polymer, g	composn of starting acid chlorides[d]				composn of excess and chlorides[d]		% reesterification	composn of acid chlorides built into polymer[d]				% holes specific for their parents
				% α	% β	mmol of α	mmol of β	mmol of α	mmol of β		mmol of α	mmol of β	% α	% β	
[Pα_1]	72[a]	265	1.0664	49.1	50.9	335	348	233	266	65.1	102	82	55.4	44.5	12.5
[Pα_2]			1.0552	49.1	50.9	178	185	77	117		101	68	59.7	40.3	20.9
[Pα_3]			1.0776	49.3	50.7	192	198	98	146		94	52	64.4	35.6	29.8
[Pβ_1]	39[b]	156	1.0423	49.3	50.7	102	105	39	37	81.3	64	68	48.9	51.1	0.81
[Pβ_2]	49[b]	193	0.9081	49.3	50.7	103	105	27	27	88.6	76	78	49.3	50.7	0.00
[Pβ_3]			0.9708	49.3	50.7	103	105	40	39		63	65	49.2	50.8	0.20
[Pβ_4]	34[b]	138	1.1798	49.3	50.7	103	105	27	22	97.5	76	83	47.8	52.2	3.04
[Pβ_5]	41[b]	152	0.8821	49.3	50.7	103	105	54	36	88.2	49	69	41.5	58.5	15.82
[Pβ_6][c] 1	50[a]	201		46.5	53.5										
2		201	0.6252	40.9	59.1	191	276	155	195	92.8	36	81	30.8	69.2	31.00
[Pβ_7]	18[b]	60	1.4348	49.3	50.7	103	105	78	63	77.6	25	42	37.3	62.7	24.34

[a] Measured by weight of combined hydrolysates. [b] Measured by quantitative infrared spectroscopy. [c] Starting β-truxinic acid 93.20%, α-truxillic acid 6.8%. [d] α = α-truxillic acid, β = β-truxinic acid.

Table III. Comparison of the Second Hydrolysis Fraction

	composn of hydrolysis fraction		
polymer	% α-truxillic acid	% β-truxinic acid	% holes specific for their parent
[Pα_2]	61.3	38.7	24.1
[Pα_3]	62.3	37.7	25.6
[Pβ_1]	48.9	51.1	0.81
[Pβ_2]	48.4	51.6	1.83
[Pβ_3]	47.0	53.0	4.67
[Pβ_4]	47.8	52.2	3.04
[Pβ_5]	42.8	57.2	13.19
[Pβ_6] 1	31.1	68.9	33.00
2	30.9	69.1	30.8
[Pβ_7]	35.8	64.2	27.38

resin could be excluded because the diastereoisomers could only be liberated by a subsequent hydrolysis, which means that they were covalently bound to the polymer and not through a complex.

α-Truxillic acid chloride (49 μmol) and 69 μmol of β-truxinic acid chloride were built into 0.8821 g of [Pβ_5]-(OH)$_2$. Thus, starting from a 49.3% α-truxillic and 50.7% β-truxinic acid chloride mixture, a residual composition of 41.5% α-truxillic and 58.5% β-truxinic acid chloride was obtained. Of the acid chloride mixture 84.2% (=41.5/49.3) is built in randomly, while 15.8% of the holes were specific for their parent, here β-truxinic acid. The resulting polymer 8 was, after washing with methanol in a Soxhlet extractor, subjected to a second acidic hydrolysis in methanol, liberating a mixture of α-truxillic acid 1 and β-truxinic acid 2. The acids were converted to their esters by treating them with diazomethane until a yellow color persisted. The composition of the dimethyl esters, determined by GC on a 3 ft × $^1/_8$ in. column filled with 20% Carbowax 20-M on Chromosorb P in the case of [Pβ_5] (Table III), was 42.8% α-truxillic acid and 57.2% β-truxinic acid. This means that 86.2% of the holes were nonspecific. On the other hand, 13.8% of the cavities were able to recognize their parents or, in other words, exhibited a memory effect.

The greater reactivity of β-truxinic acid chloride compared to that of α-truxillic acid chloride toward the [Pβ_5] polymer can be explained in three ways. (1) There is a greater intrinsic reactivity of the β derivative. (2) There is a higher energy barrier for the reaction of α-truxillic acid chloride with [Pβ_5], due to increased steric hindrance. (3) There is a washing out in the second hydrolysis of a part of the model compounds initially present in the macromolecule.

Even after several prolonged hydrolyses, only 41% of the β-truxinic acid could be removed from the initial polymer. This means that 59% of the model compounds were located in regions that were inaccessible to the hydrolysis reagents. The reaction of the polymer with the acid chloride at room temperature is not expected to change the polymer structure dramatically. Because the initial hydrolyses were repeated until no more (virtually) template assembly was split off and because the second hydrolysis was performed under less severe conditions for a shorter period of time, it is unlikely that during this second hydrolysis many of the model compounds initially buried in the interior of the highly cross-linked macromolecule were washed out.

To rule out the unexpected, we also measured the separative power of the polymer for an excess of the acid chlorides. Thus, when we treated the polymer containing cavities which were initially occupied by the β-truxinic derivative with a mixture of α-truxillic and β-truxinic acid chlorides, the excess mixture became richer in the α-derivative, and hence the amount of acid chlorides built in was richer in the β-derivative. *The number of holes specific for the β form is therefore, within the experimental error, the same, regardless of the method of determination.* This shows that the third possibility, washing out of the initially buried model compound during the second hydrolysis, does not explain the specificity of the polymer for its parents.

To test the first possibility (different intrinsic reactivities of the two acid chlorides), we synthesized polymers starting from bis(vinylbenzyl) α-truxillate 3 (Table I) with different degrees of cross-linking. The same sequence of reactions as for [Pβ_5] was carried out to test the separative power of the α polymers. Were there a greater reactivity of the β-truxinic acid chloride toward the benzyl alcohol end group in the polymer, we would expect a preference for the β form, even when using α polymers. That is not what we observed. We found instead a clear preference for the α-truxillic acid chloride when treating the α polymers with a mixture of α-truxillic and β-truxinic acid chlorides. What is more, the percentage of cavities that were able to recognize that α-truxillic acid was their parent was a function of the degree of cross-linking. If the composition of the acid chlorides built into the polymer was determined by the relative reactivities of the components, we would expect to find the same composition when using lower cross-linked copolymers. *When changing from 60 to 25% cross-linking, we observed that there was a dramatic decrease in selectivity.*

To investigate further the influence of the degree of cross-linking on the memory of vinyl polymers for their origins, we synthesized a number of β polymers with varying amounts of divinylbenzene (from 0 to 95%). The amount of bis(vinylbenzyl) α-truxinate was kept low (between 4.9 and 6.0%). With these low levels of model compound, site–site interactions are to be expected minimal,[20] and removal of the model compound will not cause important changes in the tridimensional polymer structure.

Analysis of the polymers showed that the memory of the macromolecules for their origins increased by increasing degree of cross-linking. A polymer, even under ordinary conditions, is in continuous motion, undergoing various changes in conformation.[4] The lower the degree of cross-linking the less rigid the polymer structure and the more pronounced this molecular movement. We have found that in the β polymer containing less than 15% of the divinylbenzene, there was virtually no recognition for β-truxinic acid chloride out of a mixture of α-truxillic and β-truxinic acid chlorides (Tables II and III). The few divinylbenzene bridges are not able to limit chain motions to the extent necessary to preserve the tridimensional structure of the cavities with the result that all the recognition gets lost. The stability of the holes increases with an increasing degree of cross-linking, and hence the specifity of the polymer increases.

This work showed that at least part of the cavities in our polymers were able to recognize their parents. The number of specific holes became more important when dealing with more bulky model compounds or higher cross-linked polymers.

In a future paper,[12] we describe the use of memory-containing vinyl polymers in subsequent photochemical reactions.

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Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded in KBr disks with a Perkin-Elmer 337 infrared spectrophotometer. NMR spectra were recorded on a Varian A-60 spectrometer or a Varian CFT-20 79.7-MHz NMR spectrometer. Deuteriochloroform and acetone-d_6 were used as solvents. Tetramethylsilane was used as the standard. Mass spectra were obtained with a Varian MAT Model CH7 mass spectrometer. Optical rotations were measured on a Rudolph 26202 polarimeter. Glacial acetic acid was used as the solvent. Gas chromatography was performed on a Hewlett-Packard 5710 A gas chromatograph. A Hewlett-Packard 3380 S integrator was used to weigh the relative amounts of compounds from a 3 ft × $^1/_8$ in. column. Twenty percent Carbowax 20-M on Chromosorb W or 25% Carbowax 20-M on Chromosorb P was used as the stationary phase. Irradiation experiments were done with a 450-W Hanovia medium-pressure mercury lamp.

Synthetic Procedures. α-Truxillic acid[13] and β-truxinic acid[13] were prepared according to known procedures.[21] Vinylbenzyl chloride was obtained from Dow Chemical Co.

Bis(vinylbenzyl) α-Truxillate. α-Truxillic acid 1.18 g (0.4 mmol) was suspended in water and treated with an aqueous solution of KOH until pH 8. The water was removed and the dipotassium salt was dried in a vacuum oven at 50 °C over P_2O_5 and used without further purification. To a nitrogen-flushed round-bottom flask were added 25 mL of acetonitrile, 0.80 g of 18-crown-6 ether (4 mmol), 6.3 g of vinylbenzyl chloride (40 mmol), and the dipotassium salt. The stirred suspension was heated at 60 °C for 24 h, cooled, filtered, and stripped of solvent on a rotatory evaporator. The reaction product was purified on a silica gel 60–200 mesh column. A mixture of ether and pentane was used as eluent (1/9 ether/pentane).

The monomer was further recrystallized from a 1/20 ether/pentane mixture: yield (after purification) 51%; mp 60 °C; NMR δ 4.78 (CH_2, cyclobutane protons, ABC system, H_1 at δ 3.97; H_2 at δ 4.48); δ 7.25 (m, aromatic protons); double bonds, styrene pattern (H_1 indicated the protons attached to the carbon closest to the carbonyl group).

Bis(vinylbenzyl) β-Truxinate. This monomer was prepared in a way similar to that for bis(vinylbenzyl) α-truxillate. The purification was done on a silica gel 60–200-mesh column by gradually changing the ratios of the ether/pentane mixtures which were used as eluents (1:25, 1:5, and 1:1). An automatic fraction collector was used: yield after purification 25%; mp 43 °C; NMR δ 5.17 (s, CH_2, cyclobutane protons, AB system, H_1 at δ 3.87, H_2 at δ 4.45, $J_{1,2} = 7.1$ Hz); 7.12 (m, aromatic protons); double bonds, styrene pattern (H_1 are the cyclobutane protons attached to the carbon adjacent to the carbonyl group).

Preparation of Macroporous Copolymer. The α and β polymers were synthesized in the same general way.

A solution of styrene, divinylbenzene, acetonitrile, and our monomer [bis(vinylbenzyl) α-truxillate or bis(vinylbenzyl) β-truxinate] was placed in a Pyrex tube containing a constricted neck. The tubes were degassed on a vacuum line through four consecutive freeze–thaw cycles and sealed. Heating at 75 °C for 20 h and for another 20 h at 115 °C yielded a white, hard copolymer. After being ground up with mortar and pestle, the polymer was washed in a Soxhlet extractor with methanol and toluene as solvents. The IR spectra of the polymer showed the superposition of the ester group ($J = 1730$ cm^{-1}) over the spectrum of polystyrene.

First Hydrolysis of the Polymer. A weighed amount of polymer was placed in a nitrogen-flushed, three-necked, round-bottom flask equipped with a magnetic stirrer, a reflux condenser, an addition funnel, and a gas inlet and outlet. The polymer was covered with a 1:1 mixture of HCl/CH_3OH.[5] The stirred suspension was refluxed for 24 h under a continuous stream of nitrogen, whereafter the polymer was filtered and washed with hot methanol.

The hydrolysis was repeated several times until no more model compound was released. The combined washes were evaporated to dryness under vacuum and weighed.

Rebinding Experiments. General Methods. A weighed amount of hydrolyzed polymer (±1.0 g) was suspended in 15 mL of dry ether in a dry nitrogen-flushed flask. While the mixture was stirred, an excess of a mixture of α-truxillic acid chloride and β-truxinic acid chloride is added. The composition of this mixture was previously determined as the methyl ester on a 3 ft × $^1/_8$ in. column filled with 20% Carbowax 20-M on Chromosorb W or 25% Carbowax 20-M on Chromosorb P (see first part of Experimental Section).

After 24 h at room temperature under a nitrogen atmosphere, the excess acid chloride was separated from the polymer by several washings with dry warm ether, and the acids were converted to their dimethyl esters by a 4-h reflux in methanol and analyzed by GC using the same columns. The amount of the excess was determined by weighing.

Second Hydrolysis. After the reesterification reaction, the polymer (±1.0 g) was suspended in 15 mL of methanol, and 25 mL of a 1:1 mixture of concentrated HCl in CH_3OH was added to the nitrogen-flushed flask. After an 8-h reaction at 50 °C under a nitrogen atmosphere, the polymer was filtered and washed in a Soxhlet extractor with CH_3OH for 24 h. The combined filtrate and wash fluids were evaporated to dryness under vacuum. The resulting mixture of α-truxillic and β-truxinic acids was converted to their dimethyl esters by dropwise addition of an ethereal diazomethane solution until a yellow color persisted. The composition of the resulting mixture was analyzed by GC using the columns described in the first part of the Experimental Section.

Solvent-Uptake Experiments.[18] A well-determined amount of dry polymer (±1.0 g) in an extraction thimble was placed in a flask containing enough solvent to cover the polymer in the thimble. After a certain time, the polymer in the thimble was centrifuged for 30 min and weighed immediately. After being dried in a vacuum oven at 50 °C to constant weight, the polymer was weighed again. The difference in weight of the polymer immediately after centrifugation and after drying to a constant weight represented the absorbed solvent. After being centrifuged, the polymer was almost free-flowing, and therefore we did not correct for interstitial solvent.

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Registry No. 1, 490-20-0; 2, 528-34-7; 3, 72939-12-9; 4, 72939-13-0; 6, 37597-30-1; 7, 57194-71-5.

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