

Recent Research in Polymer Chemistry

C. G. OVERBERGER

University of Michigan, Ann Arbour, Michigan, U.S.A.

I am very pleased to have this opportunity to address the Natural Rubber Conference here in Kuala Lumpur. I am particularly grateful to the Organising Committee and to Mr. Sekhar for this opportunity to report on some recent research in macromolecules. The topics to be discussed will include others than those that have something to do with natural rubber.

I think it is important for us all to recognise that rubber, particularly natural rubber, was a focal point for the beginnings of macromolecular science many years ago. Natural rubber, along with cellulose, was one of the first materials to be recognised as a large molecule. Natural rubber was one of the first macromolecules to be accepted by the classical organic chemist as an example of an organic molecule that was not cyclic, but consisted of long chains of specific structure. Thus, we have natural rubber to thank in many ways for stimulation of the tremendous growth of macromolecular chemistry as we know it today. It plays an important role whether we are talking about natural or synthetic rubber.

The area of macromolecules, whether it be science or application, is growing extremely rapidly—it is one of the largest growth areas in chemistry today—and I think there are really two reasons for this. One is that the industrial complex, because of its interest in the many new useful materials which are available, has carried out an enormous amount of research and development in this area. Secondly, the very striking situation occurs nowadays that the same problems important in synthetic macromolecules (*i.e.*, the determination of total structure and stereochemistry) are exactly the same problems that the biochemist and molecular biologist are attacking in natural polymers. Scientists who are interested primarily in

structure—the primary and secondary structure of macromolecules—are stimulating growth. Thus we have these two major factors which I think are responsible for the prodigious efforts to-date. The detailed structure of macromolecules is now being studied with the extensive use of modern instrumentation.

THREE MAJOR AREAS IN MACROMOLECULAR RESEARCH

Graft and Block Copolymers

What I would like to do today is to treat three problems—if time allows. One of these is the problem which has not particularly arisen from research in our laboratory but has been primarily an area of industrial research, although academic to some extent as well, namely the area of graft and block copolymers. This subject is now twenty years old and was pioneered primarily by academic people such as [Sir Harry] MELVILLE (1950) who is in the audience here today. I want to show you some recent data which was presented by Phillips Petroleum Company (HSIEH, 1968) on anionic block copolymers. These copolymers are, for the most part, elastomeric and it is for this reason that I would like to say a little about what has been done and what can be done with skilled techniques and an understanding of the nature of the reaction itself.

I do not want to review polymerisation of dienes, or monomers with organo-metallics or organo-lithium compounds. One recalls, however, that polymerisation with alkyl lithium initiators was a laboratory curiosity a few years ago. Today about 450 000 tons of polymer are produced annually with these initiators. The excitement of discovering that isoprene could be polymerised in pure hydro-

COMMUNICATION 513

Type	Typical Segment
A-B	AAAAAAAA-BBBBBBBBBB
A/B-B	AAABABAAB-BBBBBBBBBB
A-B-A	AAAAA-BBBBBBBBBB-AAAAA
A-A/B-A	AAAA-BBABABBBBA-AAAA
A/B-B-A/B	ABAAABA-BBBBBBBB-BAAABA
A-B-C	AAAAA-BBBBBB-CCCCC
A/B-C	AAABABBAABAB-CCCCC
(A-B) _n	AAA-BBB-AAA-BBB-AAA-BBB

Figure 1. Block copolymers, listed according to type.

carbon solvents to high *cis*-1,4-polyunsaturation certainly played an important role in the activation of intensive research on alkyl lithium initiated polymerisations. The understanding that an ion pair could be a living system (SZWARC, 1956), which could add on additional monomer units and produce blocks also, was a very important part of the development of the use of organic reactions of this kind to prepare new elastomers.

Figure 1 shows the different block copolymers according to type. This work was reported by [Dr. Henry] HSIEH (1968) at the Gordon Research Conference this summer and he has given me permission to quote some of his data. You see the first type which is a simple AB type block copolymer. This AB type of copolymer can be conveniently prepared by using a mono-metal initiator such as butyl lithium, with addition of monomer B after A is completely polymerised. Vinyl monomers containing functional groups such as methyl methacrylate and acrylonitrile may terminate the living end and may or may not initiate polymerisation of a second unit. However, these monomers can be used as monomer B to form an AB type of block copolymer by adding and polymerising monomer B at very low temperatures. These monomers polymerise very rapidly at -20 to -70°C with little termination. At higher temperatures the polar groups react with carbon lithium bonds and quickly terminate the polymerisation reaction. Now the second type is a variation of the AB type, in this case monomers A and B are polymerised randomly initially, and then monomer B is added subsequently. A similar type can also

be prepared from a monomer mixture which will be discussed later.

The ABA block copolymers can be prepared in a number of ways and the specific interest in a type of elastomer derived from ABA type will be mentioned in a subsequent talk. One can use a non-metal initiator to form an AB block copolymer first, and then couple the living end with an active difunctional compound such as dihalide or diisocyanate. These coupling reactions are well-known for simple organo-metallic compounds. The third method would be to use an initiator which would yield polymer anions propagating at two ends, *i.e.*, a bi-anion, so that each increment of monomer after the first forms two block initiators such as dilithyl butane, lithium isoprene adduct, lithium naphthalene adduct, or a complex of sodium or potassium with naphthalene, biphenyl or methyl styrene. The ABC block copolymers have three chemically dissimilar segments which are joined end to end. Here again monomers such as acrylonitrile are usually used in the last increment.

In the type (AB)_n, as the block length becomes smaller and smaller, the polymer becomes more nearly a kind of alternating copolymer. An (AB)_n type can be prepared by incremental addition of monomers alternating between A and B repeatedly either using a mono- or di-metal initiator. However, trace impurities in monomers which will terminate chain growth is the limiting factor in the success of this reaction. Generally, the process rarely exceeds more than five to seven successive increments. A better way to make this type of block copolymer is first to make a relatively low molecular weight ABA type having two active ends and then to couple this living, block copolymer with a difunctional compound. Polymers have been made with active ends as high as twenty using this particular type of technique. Under certain conditions some monomer mixtures polymerise anionically directly to block polymers because of a feature of the kinetics of this reaction. For example, in hydrocarbon solutions of butyl lithium, styrene polymerises more rapidly than does butadiene; when a mixture of butadiene

and styrene is polymerised, the living polymer anions are rich in butadiene until late in the reaction whereafter the styrene content suddenly increases. This kind of inversion phenomena is not uncommon in anionic polymerisation, *i.e.*, styrene homopolymerises faster than butadiene and yet in a mixture, butadiene is preferentially polymerised first. The understanding of this is not too difficult because of the differences in cross-propagation termination rates. I will not discuss this topic here. I simply want to illustrate that a technique or idea carried out many years ago to make new kinds of polymers provides many interesting kinds of elastomers particularly when B is a butadiene block and A is a styrene block in an ABA polymer. We could cite other similar products obtained by changing polymer structure with organic methodology of the type illustrated in the preparation of the ABA block copolymers.

Polymers as Catalysts for Organic Reactions

The second topic I should like to say something about is the use of polymers as catalysts for organic reactions. This is an area which has not had an extensive amount of work devoted to it until quite recently. It is an area in which we are personally interested and I should like to very briefly show you an outline of this kind of problem because I think it is illustrative of the kind of research which you will see in the future. The background of this particular problem did come in part from biochemistry. It is an interesting fact that in all proteolytic enzymes, enzymes whose specific function is to catalyse the hydrolysis of an ester or an amide, that the imidazole ring is involved. Histidine is a basic amino acid which contains the five-membered imidazole ring. Indeed chemists, particularly kineticists, recognised many years ago that imidazole itself was a useful catalyst for hydrolysing esters. In a macromolecule like α -chymotrypsin, which has a molecular weight of about 24 000, there are only two histidine residues and it is thought at the moment that only one of these imidazoles is responsible for the process by which this enzyme hydrolyses an ester. It is also known that an OH group from serine, another amino acid ($\text{OH}-\text{CH}_2-\text{CHNH}_2-\text{COOH}$), is necessary.

There are about 24 serine molecules in α -chymotrypsin and the evidence is fairly overwhelming that only one of these OH groups is involved in the actual process by which the ester is hydrolysed. We have synthesised polymers that are catalysts, in most cases much poorer catalysts than enzymes; in other cases we have polymers which are excellent catalysts under different conditions than enzymatic conditions.

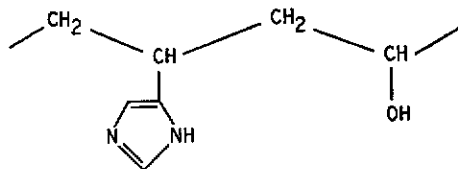


Figure 2. (a) Vinyl imidazole, copolymerised with vinyl acetate, to give a macromolecular structure containing imidazole and OH groups in random array.

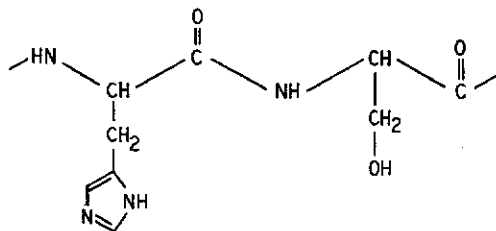


Figure 2. (b) Copoly (L-histidine-serine) having the classical peptide chain.

As an example, we made a monomer, vinyl imidazole, and copolymerised it with vinyl acetate. The acetyl group is easily removed (in fact, the imidazole helps this group to be removed) and we have then, in this case without regard for stereochemistry or secondary structure, a macromolecule containing imidazole groups and OH group in a random array [Figure 2(a)]. Katchalsky of the Weizmann Institute had copolymerised histidine and serine (KATCHALSKY *et al.*, 1960) and made a synthetic polymer having the classical peptide chain [Figure 2(b)]. When he had used this polymer to try to hydrolyse an ester like *p*-nitrophenyl acetate, he did not observe any catalytic activity. That does not mean the ester does not hydrolyse but, when I say catalytic activity, I mean a rate of reaction

above that attributable to the molar concentration of imidazole groups that are present in the copolymer. That is exactly what happened in our case as well, but fortunately Dr. N. Vorchheimer (OVERBERGER AND VORCHHEIMER, 1963), who first worked on this problem, decided to carry out some reactions at a higher pH. This copolymer was found by Dr. J. Salamone (OVERBERGER *et al.*, 1967) to be an effective catalyst for hydrolysing an ester at higher pH.

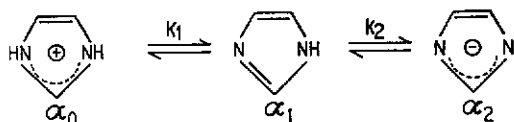


Figure 3. Imidazole and its ionic forms.

The pK_1 for imidazole is about 6.6. The pK_2 for the anionic form of imidazole (Figure 3) has never been measured because it is too high, probably about 14—it is a very weak acid. However, the neutral and anionic species must be considered when one scrutinises problems in catalysis with polymers having imidazole groups attached to them.

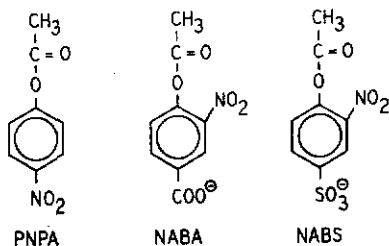


Figure 4. Phenol ester substrates.

The neutral ester substrate used was *p*-nitrophenylacetate (Figure 4). It is easy to measure the rate of hydrolysis of this ester because it releases *p*-nitrophenolate ion and you can measure its concentration spectrophotometrically.

Now I would like to show you the kind of thing one finds if one uses an excess of the catalyst, which will be polymer in this case, and the ester *p*-nitrophenylacetate. This is an initial

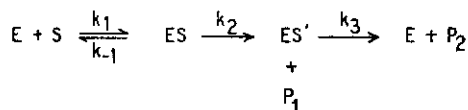


Figure 5. Hydrolysis of *p*-nitrophenylacetate by α -chymotrypsin.

rapid reversible reaction (Figure 5) and what we are measuring essentially is a pseudo second order rate constant, k_2 , which is the hydrolysis of the ester. One does these measurements in buffered solutions at constant ionic strength.

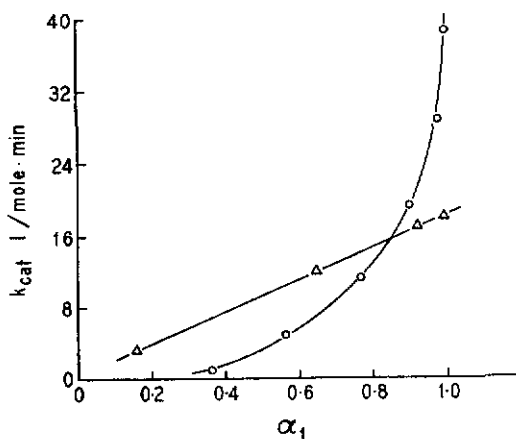


Figure 6. Solvolysis of PNPA catalysed by poly-4(5)-vinylimidazole (O) and imidazole (Δ), 28.5 per cent ethanol-water, ionic strength 0.02.

This result was the reason that we pursued the problem. You see here a plot of a derived rate constant versus the fraction of neutral imidazole residues in a homopolymer of 4 vinyl imidazole and imidazole itself (Figure 6). As you go to higher pH, the polymer begins to show catalytic activity. This polymer is not a very good catalyst but it was good enough to make us look at other things.

This is data for polyvinyl benzimidazole. If you plot a derived rate constant versus pH, benzimidazole is very uninspiring whereas the polymer shows this nice trend at higher pHs (Figure 7).

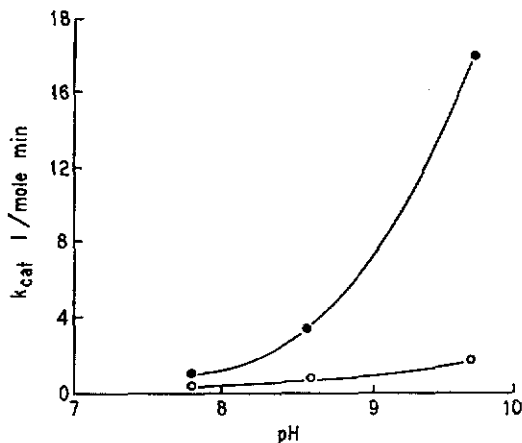


Figure 7. K_{cat} versus pH for *p*-nitrophenylacetate.

●—poly-5(6)-vinyl benzimidazole
○—benzimidazole

Now we immediately set out to prove that the anionic form of imidazole might be involved and that we were getting some kind of co-operative interaction of groups along the polymer chains. You have a neutral imidazole attacking an ester to give tetrahedral intermediate and then the anionic or neutral form of imidazole removing the proton (Figure 8). We were able to demonstrate this mechanism rather effectively. You will see in Table 1 that if you substitute the nitrogen on the imidazole

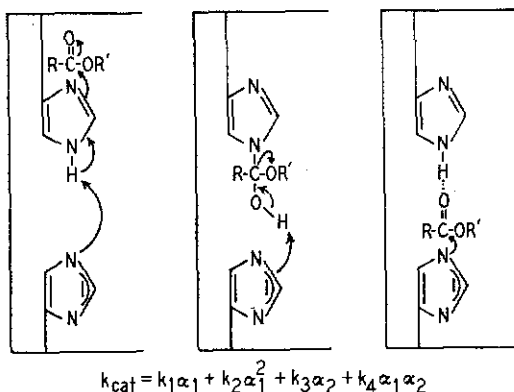


Figure 8. Mechanism of catalytic activity of imidazole groups in hydrolysis.

TABLE 1. CATALYTIC RATE CONSTANTS* OF POLY-*N*-VINYLMIDAZOLE AND POLY-2-METHYL-*N*-VINYLMIDAZOLE WITH PNPA

pH	Poly- <i>N</i> -vinylimidazole	Poly-2-methyl- <i>N</i> -vinylimidazole
7.2	3.0	0.5
8.0	3.5	0.5
9.2	3.5	0.5

* k_{cat} , 1/mole min

so that you have poly-*N*-vinylimidazole or poly-2-methyl-*N*-vinylimidazole and you measure a derived rate constant at different pH, the results are very uninteresting. There is no catalytic activity. The data tend to convince one that either you should have the anionic form of imidazole if you are going to have any catalysis, or that if two neutral imidazole groups are involved, steric factors are very important.

The second result which is quite revealing is shown in Table 2, which lists a summary of activation parameters. Here is described the work of Professor Bruice (BRUCE AND BENKOVIC, 1964) on imidazole itself on hydrolysing *p*-nitrophenylacetate. Here are described the kinetic activation parameters for a homopolymer of 4(–5) vinyl imidazole. Notice the very large entropy values (48.7 e.u.) — very indicative of the fact that you have got a random chain of some sort which has to snap into place appropriately to form rigid specific transition states or intermediates which are giving rise to catalysis. Organic chemists like to see this kind of data because it makes them think that the mechanism they are suggesting might be right.

If we put an acid group on the substrate we complicate the problem because we add an electrostatic component to the total velocity constant and we get bell-shaped curve of this kind (Figure 9). If we use, e.g., the sulphonic acid substrate or the carboxyl substrate (Figure 4), at about the pH where there is no

TABLE 2. ACTIVATION PARAMETERS FOR CATALYTIC SOLVOLYSIS OF PARA NITROPHENYLACETATE

Catalyst	Source	ΔH^* , K _{cal}	ΔF^* , K _{cal}	$T\Delta S^*$, K _{cal}	ΔS^* , e.u.
Imidazole	Bruice	7.0	17.7	-10.7	-35
Poly-4(5)-vinylimidazole	Present work	3.7	17.3	-14.6	-48.7
Poly-N-vinylimidazole	Present work	8.7	19.5	-10.8	-36
N-methylimidazole	Present work	8.3	18.8	-10.5	-35

* Activation parameters

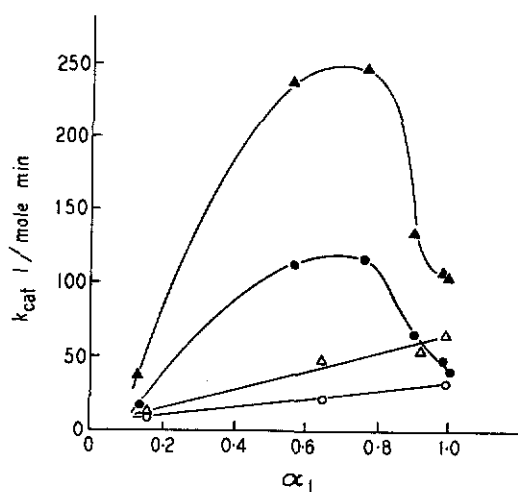


Figure 9. Dependence of the catalytic rate constants for the solvolyses of NABA and NABS catalysed by poly-4(5)-vinylimidazole ($\bullet$, $\blacktriangle$) and imidazole, ($\circ$, $\triangle$), respectively, on the fraction of neutral imidazole functions; in 28.5 per cent ethanol-water, ionic strength 0.02.

more protonated imidazole left, the carboxyl or sulphonic acid group is no longer strongly attracted by ion pair formation and the rate drops. Notice that this is a true polymeric effect. With imidazole itself, you do not see any of the electrostatic contribution to the total velocity constant. Now we have made many copolymers, studied them carefully and we have systems which are catalytic in which the rates under hydrophobic conditions are 10 000 times faster

than simple monomeric imidazole. We are not duplicating enzyme reactions, but we are simply finding out that polymers can be very useful for catalysing organic reactions and in particular we describe here the hydrolysis of esters (Figure 10).

Synthesis of New Materials for Use at High Temperatures

I would now like to discuss, briefly, a third topic which has been emphasised considerably in the last eight years and that is the synthesis

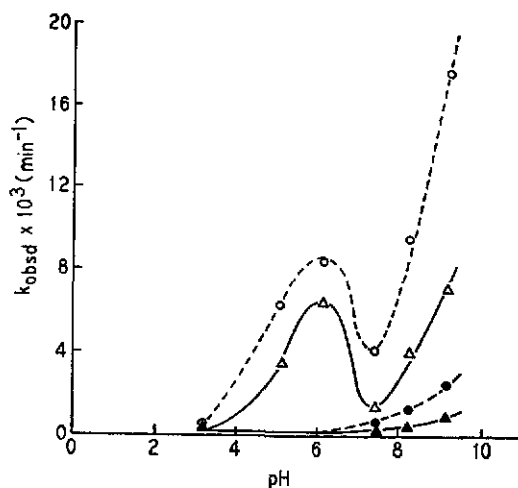


Figure 10. Profiles of pH-rate for the solvolyses of NABA and NABS catalysed by 1:1.95 copolymer of 4(5)-vinylimidazole and p-vinylphenol ($\triangle$, $\circ$) and imidazole ($\blacktriangle$, $\bullet$), respectively, in 80 per cent methanol-water, $\mu = 0.02$.

of new materials for use at high temperatures. In general these materials have not been elastomers. There are a few single rules that you should think about. The process of polymer degradation is primarily a rate process of some kind. If we take molecules of polyethylene and convert to the liquid state (assuming that no oxygen, no light or no water is present), eventually reaction will occur as these molecules collide. If we assume that all the molecules are saturated, there will be an activation energy to this degradation process, *e.g.*, perhaps 4-centre reaction that gives off hydrogen. The activation energy for this rate process will probably be a little less than the bond energy of the carbon-carbon bond, *i.e.*, the activation energy for this rate process will not be 80 kcal or so but nearer 70 kcal. On the other hand, if we admit oxygen, water or light, we all know that we must contend with rate processes of activation energy. An autoxidation via a radical chain reaction has an activation energy which can be down around 35 kcal/mole. If we have a hydrolysis reaction the activation energy will also be of that order of magnitude. The type of internal nucleophilic displacement reaction, *e.g.*, in silicone degradation, that results in 'peeling off' of monomer units will have an activation energy much lower than the theoretical bond energies involved. It does no good to say that a phosphorus nitrogen polymer will make a good high temperature polymer because the bond energy is 130 or 110 kcal/mole, since rate processes are going to dictate that this molecule will degrade at a much lower temperature than the theoretical bond-breaking temperature*. The organic chemist has known intuitively for a long time that if he immobilised the chains and keeps the material from becoming a liquid, he has a way of minimising degradation rate processes to some extent. For the past fifty years, chain stiffening

was accomplished primarily by cross-linking with covalent bonds. I want to review briefly an area that many chemists have contributed time and energy to recently — namely, the synthesis of polymers which have rigid chains, usually polyaromatics or polyheterocyclics. They may or may not be crystalline polymers.

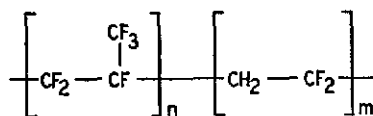


Figure 11. Viton 1.

The polymer shown in Figure 11 is a thermally stable elastomer due to the fact that by replacing hydrogen with fluorine we can increase the activation energy of the radical displacement reaction which gives rise to radical chain decomposition via a hydroperoxide. It has some elastomeric properties by virtue of that side chain CF_3 group, and is a commercial product.

Figure 12 also describes a commercial product from pyromellitic anhydride and 4,4'-diaminodiphenyl ether. The polymer is not a cheap material, but over 500 000 lb/year are made at the present time and the price will be

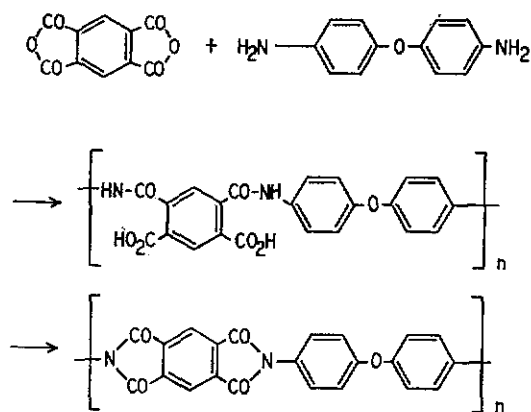


Figure 12. Rigid chain polymer, from pyromellitic anhydride and 4,4'-diaminodiphenyl ether.

*Generalised equation for Reaction Rate:

$$k = Ae^{\frac{-E}{RT}}$$

- (1) k = rate of decomposition; should be minimised to increase stability; make A as small as possible and E as large as possible.
- (2) As E increases, the thermal stability of the molecule increases, but in some cases A also increases at the same time.

reduced eventually. You may use this as a wire coating, as a film or as a moulding powder. Notice that its chain contains aromatic structures and is rigid. When you finally form the imide structure it is virtually insoluble in most solvents but can be dissolved in concentrated nitric acid and reprecipitated. Its Achilles' heel, however, is strong base or hydrazine addition to the carbonyl group—a relatively low activation energy rate process.

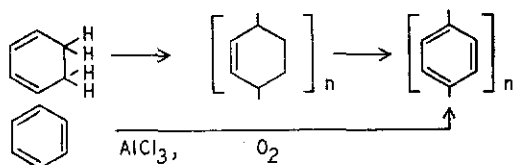
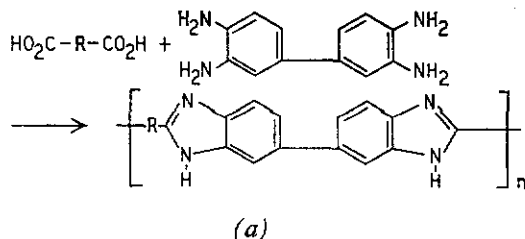


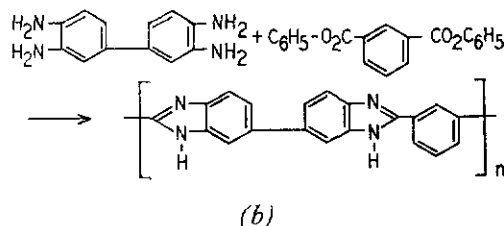
Figure 13. A polyphenyl from cyclohexadiene or benzene.

You ask: why don't you make a polyphenyl (Figure 13)? The preparation of this polymer has been reported by several workers (GOLDFINGER, 1949; HELLMAN *et al.*, 1955; PARINI AND BERLIN, 1958). One method was by the polymerisation of cyclohexadiene followed by dehydrogenation (MARVEL AND HARTZELL, 1959; CASSIDY *et al.*, 1965). KOVACIC AND KYRIAKIS (1962), at the Case Institute of Technology, used a cationic type polymerisation along with an oxidising agent like cupric chloride and was able to obtain a low molecular weight polyphenyl. He also demonstrated that his product was probably not very branched however, the polymer is very insoluble. It is a brickdust-like material that has great stability but, unfortunately, no one has yet found out how to process it.

Polybenzimidazole was prepared initially by VOGEL AND MARVEL (1961) via an exchange reaction as indicated in Figure 14 followed by milling the solid polymer in the dry state to increase the molecular weight. One can obtain intrinsic viscosities of from 3 to 4 in this way. With isophthalic acid one can obtain sufficient solubility to spin fibres from solution [Figure 14(a) and (b)]. If any of you had seen Professor Marvel in the last three or four years, you



(a)



(b)

Figure 14. Polybenzimidazole prepared in different ways.

would have noticed that, when he gives a lecture on this material, he wears a vest made from the fabric which has a red tinge to it, as the polymer is coloured. It is a useful high temperature material. Operating temperatures in oxygen at 400°C for limited periods of time are possible with fibres or films of this material.

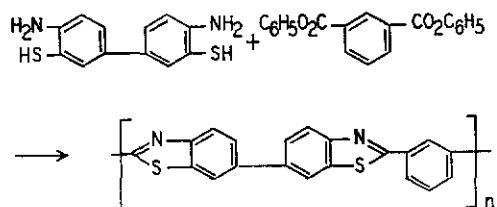


Figure 15. A type of polybenzothiazole.

I have some 150 references to polymers related to this type. I will describe a few of these briefly—Figure 15 shows a polybenzothiazole which is also quite stable. The principles are the same—no site for a rate process to occur, high rigidity to keep the molecules motionless as long as possible.

Figure 16 shows a polybenzoxazole developed by Toyo Rayon Company (YODA, 1968).

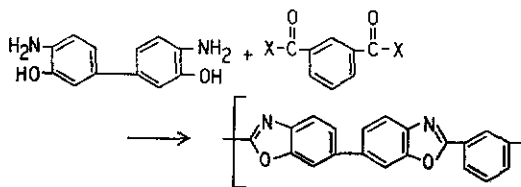


Figure 16. A type of polybenzoxazole, produced commercially.

All of these materials are virtually insoluble in the final state of polymerisation except in concentrated acids. The best procedures are to use the pre-polymer, and then carry out the final polymerisation *in situ*.

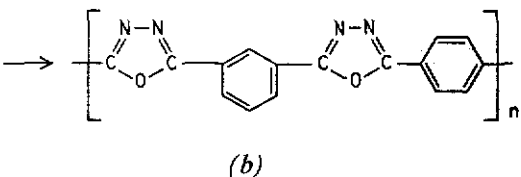
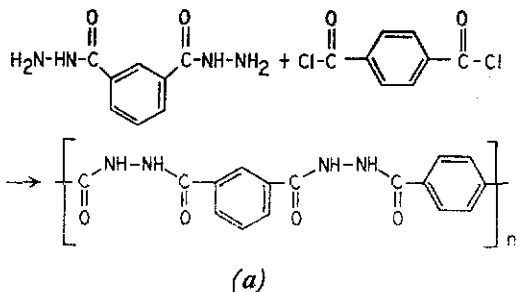


Figure 17. (a) polyhydrazide preparation for fibres. (b) oxadiazole ring formation on slowly heating the fibre.

Polyhydrazides as in Figure 17 (a) have been investigated as fibres. They have fairly high melting points. If you do it right, you can make a polymer that does not cross-link, spin it into a fibre and then, as Frazer (FRAZER AND WALLENBERGER, 1964) of Du Pont reported, the fibre itself may be heated slowly to remove water. In Figure 17 (b) you will see the structure formed, an oxadiazole ring.

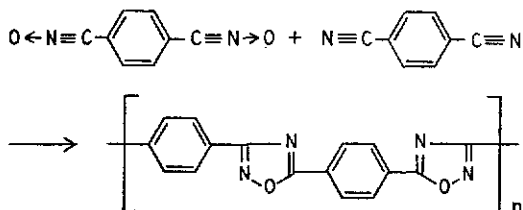


Figure 18. A polymer formed of a di-nitrile-N-oxide and a di-acetylenic compound.

The polymer has alternating oxadiazole and benzene rings and has good high temperature properties. The process of heating the fibre must, however, be a carefully controlled experiment.

Figure 18 shows a polymer that OVERBERGER AND FUJIMOTO (1965) reported a few years ago. Di-nitrile-N-oxides react with di-acetylenic compounds or di-nitriles to yield polymers that do not have quite as good thermal properties as some which I have previously described. Secondly, the preparation of starting materials is rather difficult.

There have been strong suggestions that if a ladder polymer which was highly aromatic was made, then the chain would be so stiff that it would not be soluble. I have listed here several ways in which ladder polymers can be made:

- (1) equilibrium method;
- (2) 'zipper' method;
- (3) closing cyclic polymers;
- (4) tetrafunctional monomers; and
- (5) ionic bonding.

I would not be able to discuss here all these procedures; there is only one example of the first way described. The second way is the easiest and poorest way to make a ladder. The third way utilises a cyclopolymer. The fourth procedure uses tetrafunctional monomers and one can prepare very high melting, highly heat-resistant materials.

Figure 19 shows the one classical example of a ladder from the hydrolysis of a trifunctional silane. The details of this have not been published, but have been reported by BROWN *et al.* (1960). It is an interesting case because ordina-

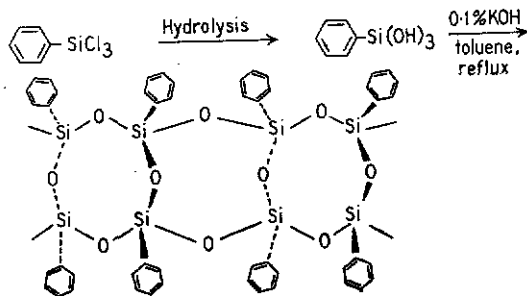


Figure 19. Ladder polymer prepared from phenyl trichlorosilane.

rily when one hydrolyses a trichlorosilane one gets cross-linked gel structures. We know this happens with the methyl derivatives but with the phenyl derivatives, one gets a ladder which has some solubility in benzene.

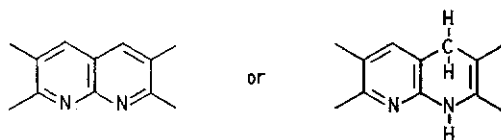


Figure 20. Black Orlon obtained from polyacrylonitrile.

Figure 20 shows the classical black Orlon obtained by heating a fabric of polyacrylonitrile under appropriate conditions to give an aromatised structure. Obviously, it is not a perfect ladder but is a kind of graphite-like material, with some cross-linking occurring. Figure 21 illustrates a mechanism for its formation.

Figure 22 is polyacrolein which is another case of a ladder type structure.

Figure 23 (a) shows a ladder structure derived from an elastomeric material. If you were to take isoprene and polymerise it all through the 1,2 bond and then cyclise it, you would have a ladder structure. You can raise the transition temperature to 140°C—thus, there is some application of this procedure with dienes [Figure 23 (b)]. Figure 24 (a) to (e) demonstrates the use of tetrafunctional mono-

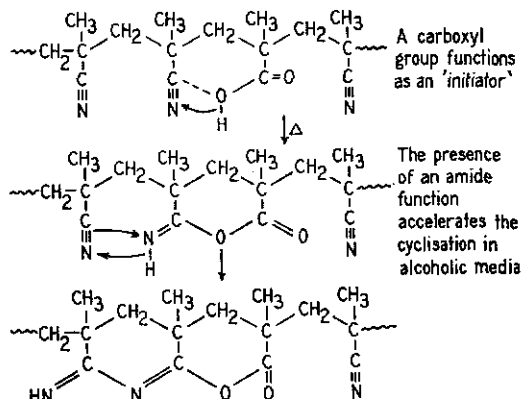


Figure 21. Thermal cyclisation of poly(methacrylonitrile). See GRASSIE AND MCNEILL (1958).

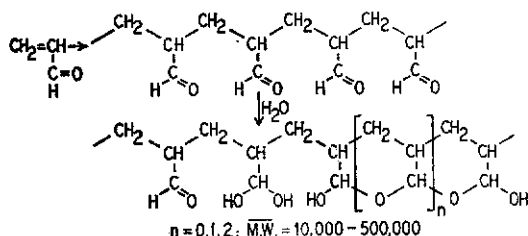
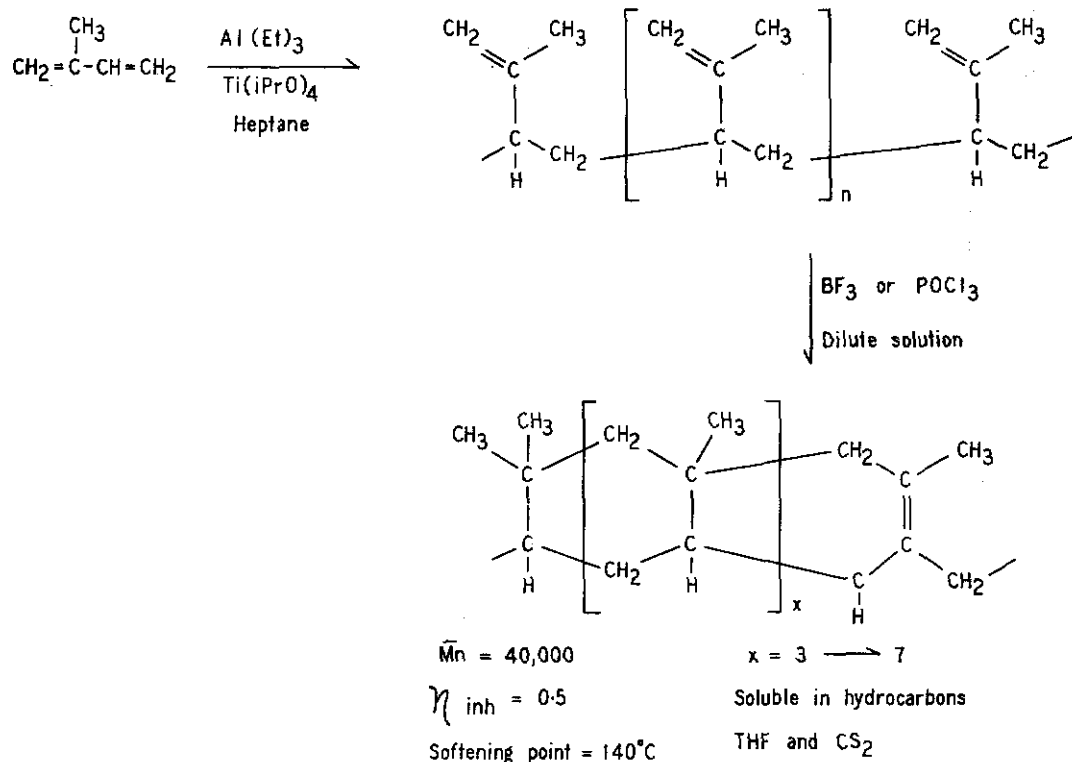


Figure 22. Ionic polymerisation of acrolein. See SCHULZ (1964 and 1965) and SCHULZ AND KERN (1956).

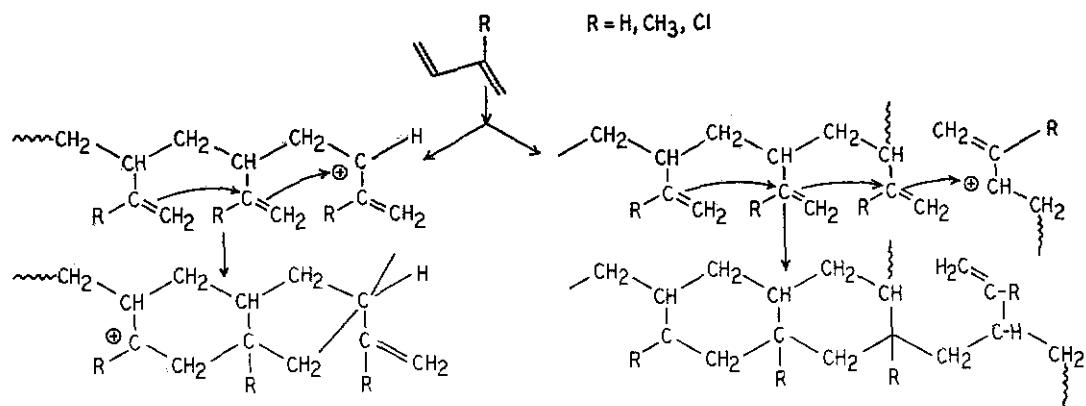
mers which under carefully controlled experimental conditions can give ladder polymers *in situ*.

CONCLUSIONS

We have discussed this morning three areas of very active research in the field of macromolecules. I selected them for mention because I think they are illustrative of what people are doing in trying to utilise large molecules. The first of these was a report of the syntheses of specific block copolymers designed as elastomers—work reported recently by Phillips Petroleum Company (HSIEH, 1968), but other companies have been involved as well. Some of these ABA type materials (styrene-butadiene-styrene) are extremely interesting elastomeric



(a)



(b)

Figure 23. (a) Ladder polymer formed by cyclisation of poly-3,4-isoprene. See DU PONT (1963). (b) Mechanism of poly(diene) cyclisation. See GAYLORD *et al.* (1964).

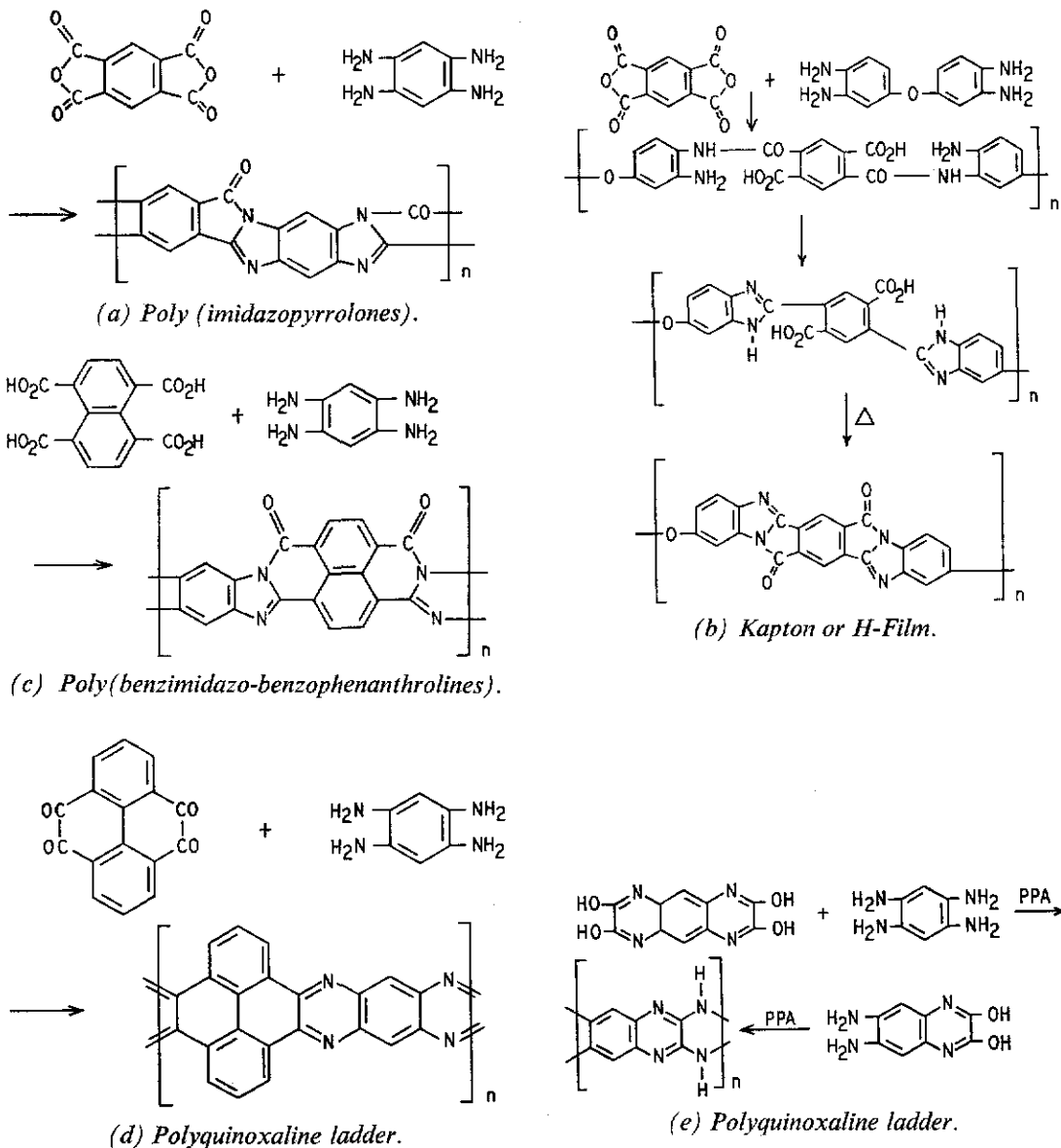


Figure 24. Ladder polymers from tetrafunctional monomers.

materials. The second topic might appear to be a rather academic problem—the use of polymers as catalysts for specific organic reactions. I picked out ester hydrolysis because it is a reaction with which we have had some ex-

perience. The basic idea of utilising detailed sequence structure for specific catalysis will have, I think, greater and greater impact on the use of polymers in catalyses in organic chemistry. Finally, I reviewed, much too briefly,

the high temperature polymer effort which is now beginning to diminish in intensity. The important thing is to recognise that we have a whole family of new, expensive polymers that will eventually find some use. As the monomer price goes down and somebody finds a good use for the polymer, they will become more and more of interest to the material user.

It has been a privilege to give this general review and I am very pleased that you listened as elastomer chemists to a few non-elastomeric topics. As I said initially, we all do the same kind of chemistry whether we are interested in natural rubber or synthetic macromolecules. I urge Malaysia to develop a strong polymer technology, to broaden their scope beyond the field of natural rubber.

REFERENCES

- BROWN, J.F. JR., VOGT, L.H. JR., KATCHMAN, A., EUSTANCE, J.W., KISER, K.M. AND KRANTZ, K.W. (1960) Double chain polymers of phenylsilsesquioxane, *J. Am. chem. Soc.*, **82**(23), 6194.
- BRUCE, T.C. AND BENKOVIC, S.J. (1964) The compensation in ΔH^* and ΔS^* accompanying the conversion of lower order nucleophilic displacement reactions to higher order catalytic processes. The temperature dependence of the hydrazinolysis and imidazole-catalyzed hydrolysis of substituted phenyl acetates. *J. Am. chem. Soc.*, **86**(3), 418.
- CASSIDY, P.E., MARVEL, C.S. AND RAY, S. (1965) Preparation and aromatization of poly-1,3-cyclohexadiene and subsequent crosslinking. III. *J. Polym. Sci. A*, **3**(4), 1553.
- DU PONT (1963) Approaches to three new polymers worked out. *Chem. Engng News*, **41**(50), 42.
- FRAZER, A.H. AND WALLENBERGER, F.T. (1964) Aromatic polyhydrazides: a new class of highly bonded, stiff polymers. *J. Polym. Sci. A*, **2**(3), 1147.
- GAYLORD, N.G., KÖSSLER, I., ŠTOLKA, M. AND VODEHNAL, J. (1964) Cyclo- and cyclized diene polymers. I. Polymerization of conjugated dienes to ladder cyclo-polymers with complex catalysts. *J. Polym. Sci. A*, **2**(9), 3969.
- GOLDFINGER, G. (1949) Polyphenyl. *J. Polym. Sci.*, **4**(1), 93.
- GRASSIE, N. AND MCNEILL, I.C. (1958) Thermal degradation of polymethacrylonitrile. Part II. The coloration reaction. *J. Polym. Sci.*, **27**(115), 207.
- HELLMANN, M., BILBO, A.J. AND PUMMER, W.J. (1955) Synthesis and properties of fluorinated polyphenyls. *J. Am. chem. Soc.*, **77**(13), 3650.
- HSIEH, H. (1968) Private communication. Phillips Petroleum Company.
- KATCHALSKI, E., FASMAN, G.D., SIMONS, E., BLOUT, E.R., GURD, F.R.N. AND KOLTUN, W.L. (1960) Synthetic histidine-containing polypeptides as catalysts for the hydrolysis of *p*-nitrophenyl acetate. *Archs Biochem. Biophys.*, **88**(2), 361.
- KOVACIC, P. AND KYRIAKIS, A. (1962) Polymerization of benzene to *p*-polyphenyl. *Tetrahedron Lett.*, 467.
- MARVEL, C.S. AND HARTZELL, G.E. (1959) Preparation and aromatization of poly-1,3-cyclohexadiene. *J. Am. chem. Soc.*, **81**(2), 448.
- MELVILLE, H.W. (1950) The chemistry of high polymers. *The Chemistry of High Polymers and Surface Chemistry* (Melville, H.W. and Rideal, E.K., ed.), New York: Chemical Publishing Co., Inc.
- OVERBERGER, C.G. AND FUJIMOTO, S. (1965) Polycycloaddition of terephthalonitrile oxide. *J. Polym. Sci. B*, **3**(9), 735.
- OVERBERGER, C.G., SALAMONE, J.C. AND YAROSLAVSKY, S. (1967) Cooperative effects in the esterolytic action of synthetic macromolecules containing imidazole and hydroxyl functions. *J. Am. chem. Soc.*, **89**(24), 6231.
- OVERBERGER, C.G. AND VORCHHEIMER, N. (1963) Imidazole-containing polymers. Synthesis and polymerization of the monomer 4(5)-vinylimidazole. *J. Am. chem. Soc.*, **85**(7), 951.
- PARINI, V.P. AND BERLIN, A.A. (1958) Nitrogenous polymers. *Izv. Akad. Nauk SSSR Otd. khim. Nauk*, 1499.
- SCHULZ, R.C. (1964) Acrolein polymers. *Angew. Chem. int. Edn*, **3**(6), 416.
- SCHULZ, R.C. (1965) Ionic polymerization of acrolein. *Chimia*, **19**(4), 143.
- SCHULZ, R.C. AND KERN, W. (1956) Acrolein polymers II. Reactions and constitution of disacryls. *Makromolek. Chem.*, **18**/19, 4.
- SZWARC, M. (1956) 'Living' polymers. *Nature, Lond.*, **178**(4543), 1168.
- VOGEL, H. AND MARVEL, C.S. (1961) Polybenzimidazoles, new thermally stable polymers. *J. Polym. Sci.*, **50**(154), 511.
- YODA, N. (1968) Private communication. Toyo Rayon Company.

DISCUSSION

Prof. Bonner asked: In connection with the catalytic activity of the synthetic polymers, you started off by mentioning the copolymers with both imidazole and OH groups and then, in your later discussions of catalytic activity, you left out the hydroxyl group. Is that significant or what happens when you put it in again?

Prof. Overberger replied: These copolymers are catalytically active; I just did not want to bore you with a lot of data. If you make that copolymer and study its pH-rate profile with the neutral substrate, you find that it is more catalytically active than the homopolymer. A particularly interesting catalyst is a copolymer from 4-vinyl imidazole and *p*-vinylphenol. Here the phenolate ion becomes quite important. These are very good catalysts because the phenolate ion is really much better than the imidazole anion in a concerted reaction. As catalysts, they are better than the homopolymer but nothing like α -chymotrypsin. To get rates in that order of magnitude, you have to get into the area of hydrophobic bonding, but that is another story.