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Panel Discussion on Thermally Stable Polymers

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Panel Discussion on Thermally Stable Polymers

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Segal: Three years ago when the Polymer Group of the Southern California Section, ACS, held its last symposium on high-temperature polymers (see *High-Temperature Polymers,* Marcel Dekker, New York, 1967) a similarly constituted, and equally illustrious, panel was asked: "Where do we go next in regard to the synthesis, characterization, and processing of thermally stable polymers?"

At that time it was agreed that completely closed ring structures would be highly desirable.

The question of the effect of partial or complete fluorine substitution on thermal stability was not resolved because of limited experimental evidence.

Physical and physical-chemical characterization of the often intractible polymers was in its infancy.

Thermal characterization was primarily limited to thermal gravimetric analysis, and there was considerable discussion about the physical and chemical composition of the samples being analyzed.

Maybe some of you on the panel and in the audience have been thinking about these things and might comment about how far we have come in three years and what we should be thinking about in the future.

Stille: I'll make a comment on this. I think we know much too little about how these polymers are degrading. We have heard here some reports of work that is beginning to elucidate some of the mechanisms of degradation. Perhaps when we know a little bit more about this, we'll know better how to design and structure polymers. Some very peculiar things have shown up recently. For example, everyone casts a jaundiced eye at the aliphatic chains in polymer systems; however, there's some evidence in our group, and in some others, that maybe aliphatic chains aren't so thermally unstable in certain situations. We've noticed thermal stabilities in polyphenylenes that are connected by alklylene chains that are not any worse than just the polyphenylene structures alone; and they don't necessarily seem to be picking up oxygen and going to carbonyl structures. They may be dehydrogenating into conjugated structures, or they may even be cyclizing into condensed ring systems. There are things like this going on during the thermal decomposition that I think we know very little about. We might benefit by some detailed studies in this regard. Also, in answer to the question of what needs to be done next, it's very possible that a better or more detailed look may be given to some of the inorganic systems. This approach seems to have been given up several years ago, but now we know a little bit more about some of the inorganic reactions and a little bit more about some of the ladder and linear systems. We might return again to some of the inorganic chains to see if we can achieve just a little better degree of thermal stability. Does anyone else have comments to this?

Levine: I'm just wondering about the stability of ladder polymers. We all say that finally the polymer chemist has statistics on his side; chain degradation must occur in two places between the rungs. I wonder if we aren't neglecting one other possibility that might be hurting us; that is, after the first break, do we know with any certainty that autocatalytic degradation is not initiated as in many polymers? Once you get your first break you then may get an unzipping reaction. What can be done along these lines to determine if this takes place? If it does, we've got serious problems with the stability of ladder structures. Of course, the unzipping sequence is dependent on the structure of the ladder polymer.

Stille: Yes, this is very true. Once you put a free radical between two rungs in the ladder, then this changes the chemistry, depending on the structure of your polymer. I would expect, in most cases, that the rail between the same two rungs on the other side of the ladder would be a little bit more susceptible to degradation. But certainly you're changing the chemistry of that second break.

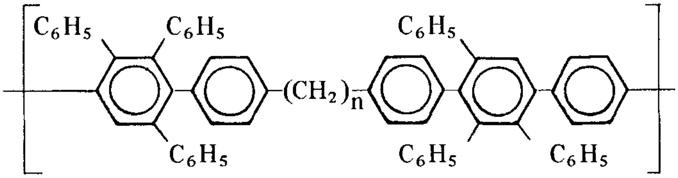
D'Alelio: I'd like to make comments regarding two aspects of Chuck Segal's question. One is on synthesis, and the second concerns the nature of the polymers to be synthesized. With regard to synthesis, I think that we've seen the beginnings of a better approach in the work of Professor Stille and others; probably the ideal way to make these polymers is by addition reactions that do not involve eliminations of any kind. Next, with respect to the polymers themselves, these addition reactions offer the possibility of closed-ring structures, some of which have been reported at this symposium. Since these polymers were shown to have high thermoplasticity and good thermal stability, this may be a direction for future research in an attempt to achieve even higher thermal stability in thermoplastic-type heterocyclic polymers. Improved processability will reduce the void content of the final fabricated product, particularly in laminated products. In fact, we might even process unfilled materials to obtain void-free structures.

Bernard Achhammer (NASA, Washington): I would like to elicit an elaboration from Professor Stille regarding the polyphenylenes. It would be nice if you could put other groups between these phenyl rings, perhaps methylene groups. Did you say there's no observable oxidation of these secondary hydrogens?

Stille: I'm not sure what's going on. When we observe the decomposition of these polymers containing aliphatic linking chains in air, we find no carbonyl bands in the infrared. Now, it may be that we're getting some dehydrogenation to form conjugated systems or cyclization resulting in polynuclear aromatic rings.

Achhammer: What type of structures are you talking about?

Stille:



where n = 3, 4, 6, 10, 14.

Achhammer: n up to 14, and you find no carbonyls?

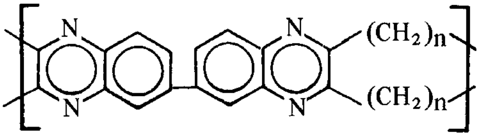
Stille: Yes, we have blocks of five phenylenes connected by the alkane unit. The decomposition temperature in air seems to begin to drop off about here (n = 10), but at least up to 6. The thermal stability is quite comparable to an all-aromatic system. At around 520°C the curves just start to break. This seems very peculiar to me, especially since we know that polyethylene decomposes at low temperatures. These polymers aren't crystalline, so there's not some nice crystalline lattice work that is preventing the diffusion of oxygen, or something like that.

Pezdirtz: Do they have any thermoplastic behavior?

Stille: These polymers have second-order transitions in the range of 150-230°C, if I remember correctly. Generally, whatever second-order transition this is, it decreases as you put more alkylene chains in.

Levine: I'd like to back up Professor Stille's comment by referring to the literature on polybenzimidazoles. In some of the work that the Russians have published, they indicate that in a homologous series, starting with succinic acid all the way to sebacic, as n increases, the T_g drops. When you reach n = 8, you have a polymer whose oxidative stability rivals that of the isophthalic moiety. This particular one (n = 8) also gives the best properties as a film or as a fiber. This work has been substantiated by Professor Iwakura in Japan working in polyphosphoric acid. He also shows data substantiating Stille: At a very high n value (Stille happens to have 14 here, Iwakura went to n = 20 or 22), this polymer had very poor properties again. The Russians have also shown that when you put a methylene moiety such as a diphenylmethane in a polybenzimidazole structure, the oxidative stability is equivalent to the polymer having the biphenyl moiety. And their evidence is quite substantial.

Stille: I've written a structure of a ladder polyquinoxaline which has a couple of pure alkylene connectors:



We've made the corresponding cyclic tetraketone, and we are going to synthesize this particular polymer and see how this ladder structure behaves thermally.

Achhammer: Is this work published?

Stille: The work on the polyphenylenes containing the alkane chains will be in *Macromolecules.*

Achhammer: Were the referees concerned about the unusual thermal stability? Have there been any changes as a result of their reading?

Stille: No. They only objected to our second-order transition temperatures.

Pezdirtz: Professor Stille, what were your criteria for stability?

Stille: The polymers were evaluated on a duPont 900 TGA at a heating rate of 3°C/min in nitrogen and in air.

Levine: I like the Russian stability data even better because they more closely approach isothermal. They kept the sample for an hour at each of various temperatures in 100°C steps, rather than the more dynamic TGA test.

William Barry (Aerospace Corporation): Did the Russians observe long induction periods for their oxidations, as in some polymers which are unchanged for long periods then degrade rapidly?

Levine: Well, this we expect. Within the framework of this test, they have substantial evidence of thermal stability. Other polymers, with different structures, are being evaluated by the same yardstick.

Gibbs: There is a substantial amount of other literature which suggests that aliphatic groups along the chain do not retain thermal stability. In one particular piece of work, that of Sheehan and others at Southern Research Institute, a series of alkylene-linked thiazole polymers were studied intensively for their fiber-forming characteristics, along with their thermal stabilities. They found that the thermal stability with one, two, or three methylene groups between aromatic rings was about consistent with that of the fully aromatic structures. When you go beyond that point, then you see more serious degradation, similar to that seen in the aliphatic hydrocarbon polymers. It's not to be thought unreasonable that these alkylene-linked polyphenyls could be forming, if the things were appropriately arranged between rings—some type of bridged alicyclic structures. I expect the steric requirements must be very seriously upheld. Professor Bailey at the University of Maryland has been preparing the completely alicyclic ladder polymers and his results would suggest that these polymers have a relatively good thermal stability. Within the whole field there is such a diversity of methods of evaluating thermal stability, not to say anything about oxidative stability, that comparisons are a very difficult problem. Each piece of data must be looked at with a great deal of scrutiny. Most people tend to trust their own results but not the results from other laboratories. This is a basic problem. The results may look good in someone else's piece of equipment, but you'll never really feel sure about it until you look at it in your own.

D'Alelio: We have also observed a similar effect on the thermal stabilities in the poly-Schiff bases when we used diamines, such as $H_2NC_6H_4XC_6H_4NH_2$, which had two benzene rings separated by a hetero atom, X. As long as the hetero atom had unpaired electrons, the stability was maintained. When we substituted a single $-CH_2-$ group for X, the thermal stability was not changed very much. We attribute some of this to the π overlap of the carbons in the benzene ring and the hydrogens on the benzene rings adjacent to the CH_2 group. When, however, we extended this bridge to four, five, or six $-CH_2-$ groups, pyrolysis and decomposition occurred, lowering the thermal stability of the polymer.

Levine: The one weakness that I can detect in the Russian work is this: As they went up in the homologous series, they got much higher inherent viscosities, which meant that they were obtaining higher-molecular-weight polymers. Consequently, it is a little dangerous to compare the stability of polymers of lower inherent viscosities with those of higher inherent viscosities. One begins to suspect more incomplete cyclization in the lower homologous series. In addition, the end groups are closer together, and these effects can become more pronounced.

Achhammer: Is there a possibility of a synergism here? The system may be degrading and cross-linking at the same time; therefore, your means of analysis could be suspect. Isn't it possible in a system like this that hydrogen could be splitting off and at the same time cross-linking the chains?

Levine: Well, is there an absolute correlation between oxidative stability and extent of cross-linking in a polymer? I don't think so.

D'Alelio: I agree with Mr. Levine. I believe there is a mechanism that is operative in these systems: The stabilities of these systems are really dependent on the binding forces, that is, cohesive energy densities between the chains which are high because of their heterocyclic structures, thereby acting as a cage or shield for these aliphatic groups. Thus, when the density of these repeating heterocyclic units is low, the aliphatic structures between them become susceptible to degradative attack.

Segal: That's somewhat consistent with the results that have been observed with polyxylylenes; they are not stable to oxidation at even moderate temperatures. In Professor Stille's polyphenylenes there must be some sort of protection provided by the pendent phenyl groups.

D'Alelio: It must be an energetic system, such as the cohesive energy density between chains.

Stille: I would have liked to invoke some sort of mechanism whereby the large phenyl bulk was protecting these alkylene groups. But I just can't see that up to n = 10, since there is very little difference between this and some of the shorter chains.

Norman Madison (Dow Chemical Corp.): Professor Bailey's mechanism of backbiting in degrading of aliphatics may not be possible with Professor Stille's polymers because of steric bulk. Bailey's mechanism must involve a cyclization which would be impossible with Stille's polymer, unless you go to (CH_2) where $n > 10$.

Stille: You're thinking of forming a benzyl radical first, and then a six-membered cyclization back? Isn't Bailey talking about a pyrolysis involving an unsaturation?

Madison: No; he's finding very consistent results with his backbiting mechanism and decomposition of polypropylene, polyethylene, and polystyrene. With your polyphenylenes you would have an almost impossible time getting the type of geometry that Bailey needs for his type of decomposition.

Gibbs: Bailey is not necessarily talking about the initiation step. You can initiate the break in Stille's polymer, for example, in between the 14 carbon atoms and still probably get Bailey's mechanism.

Stille: There isn't a lot of weight loss in the pyrolysis to account for these alkylene chains being burnt off and leaving a rather large phenyl residue which might not be volatile, or at least not very volatile.

Robert Landel (Jet Propulsion Laboratory): I have several questions. What is the effect of specimen size in TGA?

Stille: Fineness of sample can really affect the rate of decomposition of the polymers.

Levine: Not only that, but you should standardize on the sample size and container geometry, also. One of the big problems we have today is in trying to compare stability data on tests run in different laboratories. For example, in some of the work reported today, the TGA were run at 1°C/min. We run at 6°C/min, and other laboratories run them at different rates.

Landel: What do we know about kinetics? What happens when the TGA rate is changed?

Gibbs: This is a very valuable technique, perhaps the most valuable technique for looking at the degradation kinetics. You can study decomposition isothermally, of course, which has been indicated also. One valuable technique is to vary the heating rate between fairly large extremes, but this is limited in a practical way from slow rates of perhaps half a degree a minute up to 20 or 30°C/min. This allows one to spread the thermogram out and to deduce a number of kinetic parameters, and I'd rather not get into that. To the kineticist, the prime parameters are concentrations in terms of W/W_0. This leaves one a little worried, because now you've implied a concentration dependence which is not really a concentration dependence, it's a mass dependence.

Landel: What about the effect of adding pressure? What happens if you degrade in contained pressure; for example, nitrogen or in the presence of some of the decomposition products?

Gibbs: Several years ago, Jaffe from the University of Cincinnati published some work on a related problem. In a degradation which gave rise to a gaseous product, he ran the reaction in an evacuated system which was pumped continuously. In an identical reaction, the product was not removed as the reaction proceeded. The entire course of the reaction was changed.

Landel: Would this be the effect in large, thick samples where some degradation products are trapped in the sample?

Gibbs: That can also happen. There is also a problem of residence time, which is of concern in the design of the analytical instrument. How big is the hot zone, mean free path, things of this sort? You can actually get involved with sample size and momentum transfer when you work with a sample as small as a few hundredths of a milligram.

Landel: These are all questions which should be considered in investigating new polymers.

Gibbs: There's nobody that can stand up here and defend the use of TGA as an unambiguous tool to evaluate polymers. I don't think anybody here would propose to do that. And there aren't too many people who would stand up and propose the use of isothermal weight loss as a really accurate method of evaluating polymers. Generally, we don't use polymers where the only criterion is: How long do they occupy space? Usually we're more concerned with other factors such as the physical or chemical properties of the polymers. The synthetic polymer chemist tends to regard such bits of information as TGA, isothermal aging, and related tests as important but not vital elements in determining which systems have somewhat more potential than others. There's a tremendous danger here. It's a screening program where you prefer to bring along all the good candidates and drop out all the obviously bad ones.

Landel: If we've screened a large number of candidates, then the work in the future should concentrate along a more complete investigation of the most promising polymers.

Gibbs: Yes, I think that's what's happening. It's a little difficult when we only look at current development, as we have, to keep a good perspective. Now let's go back 10 years, and look at what was then the state of the art. If you analyzed the thinking of how we then approached the synthesis of a plastic-like polymer which would have a long life at temperatures around 600°F, you'd be very surprised to see the changes in thinking that have come about—since that time, both a change in thinking and the development of new experimental techniques to aid the synthetic chemist. If you look in the current literature, you'll find that most investigators who are interested in the materials that have high softening temperatures or second-order transition temperatures are concentrating on the aromatic heterocyclic polymers. If you look into other areas, such as polymers with good stability and low T_g, you'll find that they have investigated silicones, fluorinated aliphatic polymers, or fluorinated aliphatic heterocyclic-type polymers. I would hesitate to say that this was a result of a sophisticated theoretical analysis. It's a result of trial and error. Theory has typically trailed behind what the synthetic chemists are doing. I'd like to have it the other way, but it hasn't worked that way so far.

Landel: What are the things that are most needed in order to determine what these structures should be? What sort of modifications are possible?

Gibbs: The idea of going from the ladder polymer to a three-dimensional ladder polymer (triangular in cross section) has some attraction. The problem of processability is an important factor and is becoming increasingly more important in the utilization of these materials. Also, other factors, which we really haven't talked about, are the other engineering properties which make a material valuable.

Levine: Bernie Achhammer once commented that what we need are better ways of characterizing and definitely proving that we have certain types of structures. For example, we need a good method for determining the difference between 99.5 and 99.9% ring closure in the ladder polymer. Basically, almost anyone today can synthesize a thermally stable polymer; but the characterization is becoming a tougher and tougher problem as the molecules become more and more complex.

Pezdirtz: As Dr. Gibbs mentioned, very few polymers rely for their utility on just maintaining weight upon exposure to elevated temperature. I think as time goes on we should be seeing more of the type of characterization techniques as Professor Gilham described here, where you can use a small amount of material and obtain a meaningful measure of a polymer's physical response as a function of temperature, both dynamic and isothermal.

Thomas Augurt (American Cyanamid): Thermal stability may be very substantially influenced by the 0.5-1.0% residual single bonds left in the polymer. Truly two-dimensional polymers might be one of the next goals to look for, perhaps utilizing inorganic chemistry as well. The interaction of the aromatic chains in the ladder polyaromatics ought to be examined more closely. π-π, and other types of interactions, may play very important roles.

Stille: One comment to that: I might say that we've seen thermal stabilities of model compounds that are as good as the polymer. So your comment about the one weak link in perhaps 30 units is appropriate here. It may not make any difference in the TGA curve, since the 30-mer is still not volatile, but it may well make a big difference in the mechanical properties.

T. F. Yen (California State College, Los Angeles): Adamantane is a stable, diamond-like structure. Couldn't it be used as a building block for stable polymers?

Levine: Your comment on adamantane is well taken. I prefer to look upon it as a type of organic molecule which represents a workable diamond crystalline lattice. For example, any ring structure which would follow Bredt's rule would give you more stable polymers, in that they cannot undergo elimination reactions. You cannot have double bonds at bridgehead carbons. Any other ring structure would give you the same thing; there's nothing magic about adamantane.

Allan Rembaum (Jet Propulsion Laboratories): There has been some recent work done on the complexes of electronegative and electropositive polymers. I note some instances where this has led to improved mechanical properties. My question is: Would this kind of principle, if applied to already thermally stable polymers, improve their thermal stability?

Levine: This isn't new. You might consider the intermolecular hydrogen bond in just this sort of category.

Rembaum: This isn't what I had in mind. Polymeric charge transfer complexes belong to a different category.

Wolfgang Wrasidlo (Naval Ordnance Laboratory): Why have investigators like Dr. Wall (NBS) not shown interest in thermal decomposition studies with polyheterocyclics? Is there a lack of funding?

Achhammer: I think that it's pretty obvious that if we want to publish in the field of degradation of polymers, which requires that we get some answers, that we're going to deal with the simpler materials. This is the case, particularly when we are trying to understand the mechanisms and kinetics of the reactions. However, Dr. Wall has undertaken for NASA a program on the oxidation of the heterocyclic materials; i.e., pyrones, PI's, and PBI's. Dr. Wall has been working for about 6 months on these polymers. I would hope that maybe in a year he would have something to report; however, it's a very difficult problem. Some money is available, and I don't think that money is a primary factor. A current problem with the heterocyclics is oxidative stability over a long time, say, over 2000 hr.

Gibbs: There is a considerable amount of work going into the study of the degradation of aromatic-heterocyclic polymers. Some of this is conducted along with the synthesis effort. Most of it is conducted using the advantages allowed by the development over the last few years of more sophisticated instrumentation. People are no longer restricted to looking at degradation by the very gross techniques, but are able to get much closer to an understanding of the processes involved. An understanding of these complex reactions, however, has not been generally attained.

Degradation is not the only problem area. A similar situation exists in the determination of physical properties. For example, if you looked at a current issue of *Macromolecules* or the *Journal of Polymer Science,* you would undoubtedly find more solution property data reported on polystyrene than on any other single polymer system. There are active groups in nearly every laboratory that is involved in high-temperature polymers, including our own, who are looking at physical properties and publishing at rather frequent intervals. At the present we even have some questions about the polystyrene data. If you look at the literature during the next 5 to 10 years, I think that a good many of these problems will be resolved.

Certain people feel that the way to look at oxidation reactions is to begin with the very basic study of simple hydrocarbons, and work up from there. Now, if you can wait to get these simple data, and put the kinetic constants together, eventually a fairly coherent picture will emerge. But, if you're faced with coming up with a material which will be used in your lifetime, I think other considerations have to come to bear.

Achhammer: Putting materials to use at the present time is of concern. We're well beyond the state of our fundamental knowledge in some areas; for example, in laminates, where fixes and guesses must be made now and explained later. Let's presume that a laminate degrades by an oxidation mechanism. Maybe we can't prove that at the moment, but the laminates are still going to be used in aircraft and somebody's going to have to come up with some workable answers.

Levine: With regard to your comment about the laminate; there's no doubt that it's oxidation. If you take the same panel and place it in helium, it will age extremely well at elevated temperatures. The problem is *how* does it oxidize, not *does* it oxidize.

Landel: Processing and fabrication can be in themselves a research problem which a lot of people face.

Levine: That's right. Within relatively narrow limits all the aromatic heterocyclics exhibit approximately the same order of stability. The winner is going to be the most processable.

Landel: On the subject of degradation: Is there any effect of mechanical stress on the degradation process?

Levine: This has just come out very recently. The leader in this field is Bloomingdale in Havre de Grace, Maryland. They have shown that tensile shear specimens will degrade more rapidly on long-time aging if they are held under an applied stress. This is not weight-loss degradation. I think this is a very, very long-range thermoplastic phenomenon over a very long period of time. In some applications we're talking in terms of heat aging over a period of a year or two. There is very definitely evidence that under an applied stress many adhesives will fail prematurely.

Landel: That would be something different perhaps. Has anyone looked at the behavior of these materials after orientation, preferably under biaxial orientation? Will that orientation have an effect on the stability? It would seem to me that if you biaxially oriented (planes of the system with the planes of the sheet) then you might have a difference in stability. Has this question been looked at?

Pezdirtz: With most of these systems I don't think you can actually biaxially orient them, since the final films have very little flow.

Landel: At least one polymer reported by Professor Stille softened at 300°C, and decomposition set in at 520°C.

Stille: The ones with the alkylene chains in between? There's some sort of second-order transition in the range of 150-250°C depending on which particular sample it is. No, we haven't done anything with those yet.

Guy Berry (Mellon Institute): Those would be a poor choice, I think. If you look at the X-ray diagram of those, you get a spacing of around 7 Å, which I think fits in with the substituent phenyl groups. So any interactions have to be very small. You could have parallel stacking of the rod-like molecules, or on the order of that kind. The interaction which appears to be present in BBB cannot occur for this polymer.

Landel: Can you orient BBB?

Berry: We haven't been able to do it so far, to my knowledge. You can roll it out to form films, but these show no orientation.

Landel: I wonder if the panel would like to comment on the solubility of these polymers. It would seem to me that the types of solvents being investigated are routinely off the shelf. What kinds of solvents should be looked for or what kinds of solvent-polymer interaction should we look for? We had once started to look at fused salts as a solubilizing medium. There are possibilities of very strong interaction between the solvent and the polymer. There is also the possibility of the interaction of charge transfer complexes. To what extent can these kinds of very strong interactions be used as a means for solution, for characterization, or for processing?

Gibbs: You can look at the hydrogen-bonding indices, for example. You can go back to Hildebrand-Scott parameters. These are approaches which are typically used. In the systems that we have been more interested in, it appears that protonation is a very important phenomenon. I don't know what Dr. Berry's particular feelings are on this matter, but I'm sure that this is the thing that we're looking at in his particular system. You're forming a protonated species which is soluble in the system that you have. In some cases you can actually form a salt. I don't know anybody who's looked into such things as charge transfer complexes as a real means of obtaining solubility. People have looked at polyimides in a fused salt mixture. But there's a certain amount of reticence in looking at these solvents. They may be important from an academic point of view, but if a man's interested in the practical use of a material, fused salts would have a negligible value. Dr. Berry, would you care to comment on the solubility phenomenon in some of the systems that you work with?

Berry: We know that we get protonation. We tried a variety of solvents with BBB. In most of these we had an upper limit of around 200°C. The dye itself is not very soluble; you don't have to go to the polymer to find insolubility. But if you take the dyestuff you can sublime it at around 300°C. We took some silicone oil and heated it up, and kept the dyestuff in the silicone at around 400°C. It goes into solution, and as we come back down to temperature, it comes back out again. It didn't work for the polymer, but I think we're talking about reaction. If we can find a solvent which is stable and has the right kind of cohesive energy, then we can break up these π bonds at ambient temperature for BBB or polybenzimidazoles. For hydrogen bonds, you may have to use a different kind of solvent. There's really no one answer for this kind of system that you've cited.

Stille: For many of the nitrogen heterocyclics that have been made. Marvel's polybenzimidazoles, our polyquinoxalines, some of the pyrazoles, and so on, you find that the solvents which will dissolve these completely are sulfuric acid, methane sulfonic acid, and phenol for some of the polyquinoxalines. So this is one class of good hydrogen-bonding solvents for certain heterocycles that are highly polar. Sometimes, highly polar solvents will do a reasonable job on them. I think this idea of charge transfer formation has merit. Many of these aromatic systems are good donors (π donors), especially those with the nitrogen in them. If I recall, there was a paper using arsenic and antimony chloride eutectic as a solvent [H. A. Szymanski, W. Collins, and A. Bluemle, *Polymer Letters,* **3**, 81 (1965)]. These are good acceptors.

Berry: Remember that these are "polydyes"; so that you can use certain reactions which are known for dyes to achieve solubility. One such, involving the use of a reducing agent, does lead to solubility for BBB, but the solutions tend to oxidize readily, leading to precipitation of the BBB polymer. There may be a better way of obtaining similar solutions.

Stille: Relatively low-boiling acids, such as HF, have also been used. Tetrafluorodichloroacetone hydrate is reasonably low boiling and will circumvent the problems associated with sulfuric acid and phosphoric acid.

Berry: We've never gotten any of these solvents to dissolve these polymers.

Segal: I want to thank the members of this panel and today's speakers for their participation in this symposium. Several new and challenging ideas have developed here. I am sure you are all anxious to return to your laboratories to explore these ideas and to prepare for our next symposium.

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