

BLOCK COPOLYMERS

by

James Richard Gross

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1 9 7 0

STATEMENT BY AUTHOR

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

James E. Mulvaney
JAMES E. MULVANEY
Associate Professor of Chemistry

2/9/70
Date

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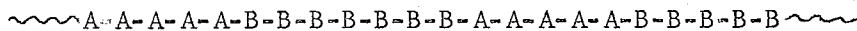
ABSTRACT

A number of monomers were copolymerized with vinylene carbonate and phenyl vinylene carbonate. These copolymers were hydrolyzed and the resulting 1,2-glycols were cleaved to form polymers with aldehyde endgroups. The aldehyde groups were either oxidized to the acid or reduced to the alcohol.

The feasibility of forming block copolymers by a carbonyl diimidazole-activated esterification reaction was demonstrated by the successful coupling of acid-terminated polystyrene with 1,4-cyclohexanediol and with alcohol-terminated polystyrene. The results of several attempts to prepare blocks by this method are promising.

INTRODUCTION

Block copolymers have been the subject of considerable research effort in recent years. Because they consist of two or more different polymers covalently bonded together, they frequently exhibit properties quite different from a blend of the respective homopolymers. A well-known class of block copolymers is the elastomeric "Spandex" fibers. In this polymer, hard fiber-forming segments alternate with soft rubbery segments as represented by 1 in which A and B are different monomer units.



1

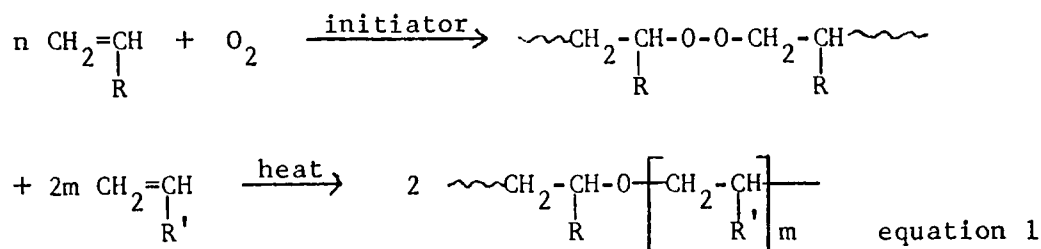
A number of methods have been developed for the synthesis of block polymers and several reviews are available (Ceresa 1965, Henderson and Szwarc 1968, Smets and Hart 1960).

One method of forming block copolymers is to rupture a backbone covalent bond of one polymer in the presence of a polymerizable monomer. Procedures used for this purpose include subjecting the polymer to cold milling, high-speed stirring, ultrasonic vibration, freezing and thawing, vapor-phase swelling, and high-voltage spark discharge (Smets and Hart 1960, Gaylord and Ang 1964, Ceresa 1965). These techniques generate free-radicals by the homolytic cleavage of covalent bonds. The radicals so formed may recombine or initiate the polymerization of a new

monomer. A trivial example of this phenomenon is seen in the brittleness of a rubber band which has been repeatedly and frequently stretched. A combination of the heat generated by internal friction and the mechanical strain of stretching produces free radicals which can then cause further cross-linking of the rubber. These additional cross-links decrease the flexibility of the rubber and cause the apparent brittleness. Heat and ultraviolet irradiation have similar effects on rubber.

Another method of generating radical chain ends on polymers is the thermal decomposition of a polymer with either peroxide endgroups or peroxide linkages in the chain backbone. If a monomer capable of radical polymerization is present, block polymer is formed. Peroxide linkages may be incorporated in polymers in several ways.

Oxygen copolymerizes with styrene, methyl methacrylate, and vinyl acetate, and these copolymers upon thermal decomposition in the presence of a second vinyl monomer (equation 1) form block copolymers (Ceresa 1960).

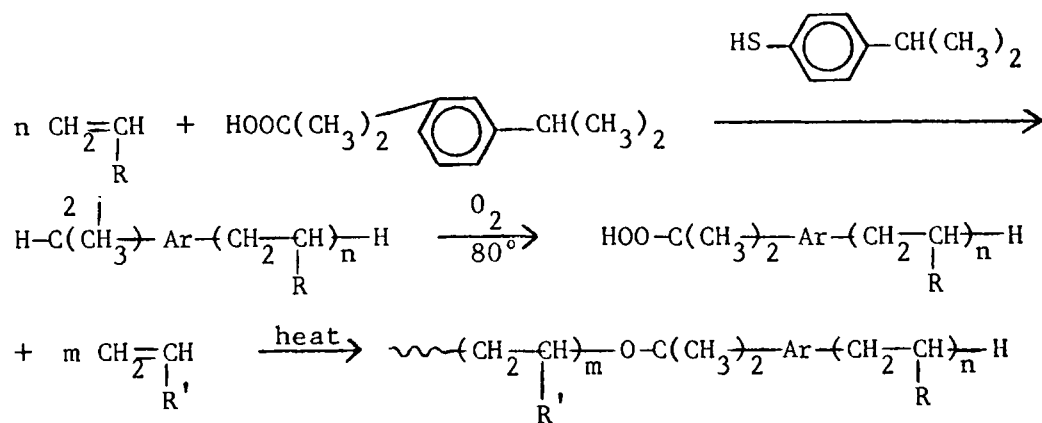


In a similar and perhaps more controllable reaction, initiation of polymerization is caused by polymeric phthalyl peroxide yielding a polymer containing short blocks of this peroxide. Thermal decomposition

of this copolymer in the presence of a new monomer again causes block polymer formation (Woodward and Smets 1955).

Peroxide endgroups have been introduced in polymers by use of bifunctional peroxide initiators and by conversion of other types of endgroups into peroxides in a separate step. An example of the former is the redox emulsion polymerization method of Orr and Williams (1956) using *m*-diisopropylbenzene dihydroperoxide. The first peroxide group of the initiator is decomposed in the aqueous phase and becomes attached to a growing polymer chain in a monomer-polymer droplet. Since the remaining peroxide group is isolated from the water-soluble redox agents, it is available for later initiation of a new monomer after isolation of the first polymer.

Isopropylaryl endgroups have been converted into hydroperoxides by Urwin (1958). Polymerization was initiated by *m*-diisopropylbenzene monohydroperoxide and cumyl mercaptan was used as a chain transfer agent. Both of these cumyl endgroups may be converted to hydroperoxides which can initiate the polymerization of a second monomer to form an AAAAAABBBBBB type block polymer as outlined in equation 2.

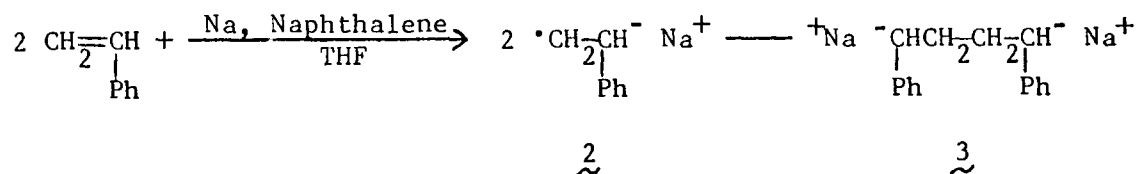


equation 2

The "living" polymer technique currently is the best method of preparing block copolymers of uniform size and sequence. A comprehensive review on "living" polymers is given by Henderson and Szwarc (1968). Usually there are three basic steps in any addition polymerization; initiation, propagation, and termination. By careful control of conditions, the termination step can be avoided in some anionic systems with the result that the polymer chains remain active for the duration of the experiment. Such active polymers are described as "living" polymers and are capable of causing the polymerization of certain new monomers. If all traces of impurities are purged from the polymerization mixture and the new monomer, this cycle can be repeated until a block polymer of the desired size and sequence has been formed. It is by no means a simple task to obtain and maintain the high degree of purity of monomers, solvents, and reaction vessels necessary for good "living" polymer preparations, and high vacuum apparatus is essential. In addition to the technical difficulties, another drawback is that not all "living" polymers will initiate the polymerization of all monomers. A "living" polymer of styrene which has styryl anions on the chain ends will initiate the polymerization of epoxides, but the alcoholate anion will not add to styrene so the process cannot be repeated to form an alternating block polymer. Some monomers are completely unreactive toward nucleophiles and this is another serious limitation.

In a typical "living" polymer preparation, anion radicals of styrene (2) are formed by electron transfer from a solution of sodium and naphthalene in tetrahydrofuran. These anion radicals then combine

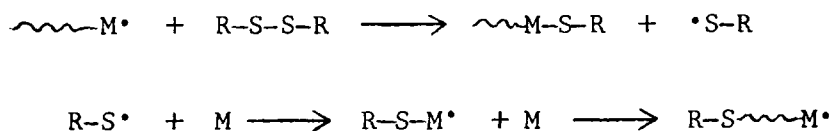
to form a dianion (3) which then adds more monomer forming a polymeric dianion.



When all of the styrene has been polymerized, the resulting "living" polymer will add new monomer to produce a "living" block copolymer.

"Living" polymers can be converted into polymers with functional endgroups. For example, treatment with phosgene produces polymers with chlorocarbonate endgroups (Finaz, Rempp, and Parrod 1962).

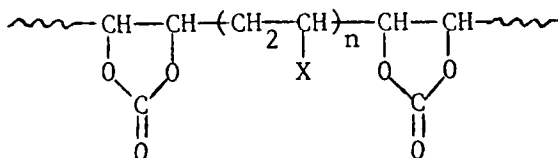
The use of chain transfer agents to place functional groups on polymers is a method which has wide potential application for a number of different functional groups. A common chain transfer agent such as a disulfide can be prepared with a variety of functional groups (Pier-son, Costanza, and Weinstein 1955). The behavior of a disulfide during a polymerization is shown in equation 3.



equation 3

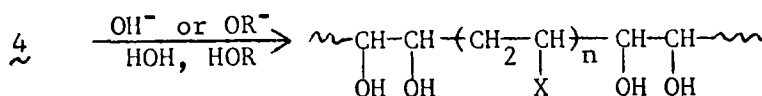
In this work a polystyrene containing carboxylic acid terminal groups was prepared via the appropriate disulfide. Furthermore, radical copolymers containing a small amount of vinylene carbonate have

been prepared. Vinylene carbonate copolymerizes with a wide variety of other vinyl monomers to produce copolymers such as 4.



4

The average value of n may be controlled by regulating the amount of vinylene carbonate in the feed. Cyclic carbonates are readily hydrolyzed to 1,2-glycols (5). Periodic acid is known to cleave 1,2-glycols to aldehyde groups (6).



5



6

The resulting aldehyde-terminated polymer (6) can be oxidized by potassium permanganate to a polymer terminated by carboxyl groups or it can be reduced by sodium borohydride to a hydroxy-terminated polymer. By using one of the various esterification methods available, a polymer with acid endgroups could be coupled to a hydroxy-terminated polymer in which the repeating group is different. The result is a perfectly alternating block copolymer in which the average length of the blocks is known.

copolymer was isolated. An uncharacterized precipitate formed during the polymerization. The copolymer of acenaphthylene and phenyl vinylene carbonate was prepared. This specific copolymer has not been reported, but Forgione (1968) prepared poly(phenyl vinylene carbonate) and suggested that phenyl vinylene carbonate was readily copolymerized with a variety of comonomers.

In order to decrease the size of the styrene blocks in the copolymer of styrene and vinylene carbonate (7) the method used by Gollmar (1969) was employed. The initial polymerization mixture contained an excess of vinylene carbonate over styrene. Twice during the two-week polymerization period, styrene and initiator were added.

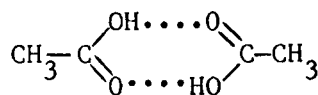
The copolymer (7) was hydrolyzed by sodium methoxide in tetrahydrofuran (THF) to yield the corresponding copolymer of styrene and vinylene glycol (8). Copolymer (8) was cleaved by periodic acid in tetrahydrofuran to yield polystyrene terminated by aldehyde groups (9). Reduction of the aldehyde groups with sodium borohydride (NaBH_4) yielded polystyrene with hydroxy endgroups (10) (see Figure 1).

Alternatively, cleavage by periodic acid and potassium permanganate in tetrahydrofuran, containing a little water, yielded polystyrene terminated by carboxylic acid endgroups (11) (see Figure 1).

Another method of preparing an acid-terminated polystyrene is to use dithiodiglycolic acid as a chain transfer agent in a radical polymerization (see equation 3). The molecular weight is controlled by the amount of transfer agent in the feed. Polymer 12 was prepared in this manner (see Figure 1).

N-vinyl pyrrolidone copolymerizes with vinylene carbonate to yield the copolymer 13. Poly(N-vinyl pyrrolidone) is very hygroscopic and in several instances, after treating this copolymer in water, the weight of absorbed water exceeded the weight of the original polymer. Drying in a vacuum oven at 75° for several days removed only a fraction of the water, which interfered with later reactions. The copolymer (13) was hydrolyzed in methanol with sodium methoxide to yield the corresponding vic-glycol copolymer (14). Copolymer (14) was cleaved in water by periodic acid and either oxidized to the acid-terminated polymer (15) by potassium permanganate or the intermediate aldehyde (16) was isolated, redissolved in dry dimethylformamide (DMF), and reduced to the alcohol (17) with sodium borohydride (see Figure 2).

The copolymer of N-vinyl carbazole and vinylene carbonate (18) was hydrolyzed (19) and cleaved to acid (20) and alcohol (21) end-groups by conditions similar to those employed for the copolymer of styrene and vinylene carbonate (see Figure 2). The copolymer (18) was of low molecular weight, η_{inh} in benzene 0.105 at 0.5 g/dl. Cleavage of 18 to the acid-terminated polymer (20) resulted in a viscosity increase, η_{inh} 0.152. Intermolecular hydrogen bonding may account for this increase as the alcohol-terminated polymer (21) had η_{inh} 0.079. Acetic acid is known to form a dimer (22).



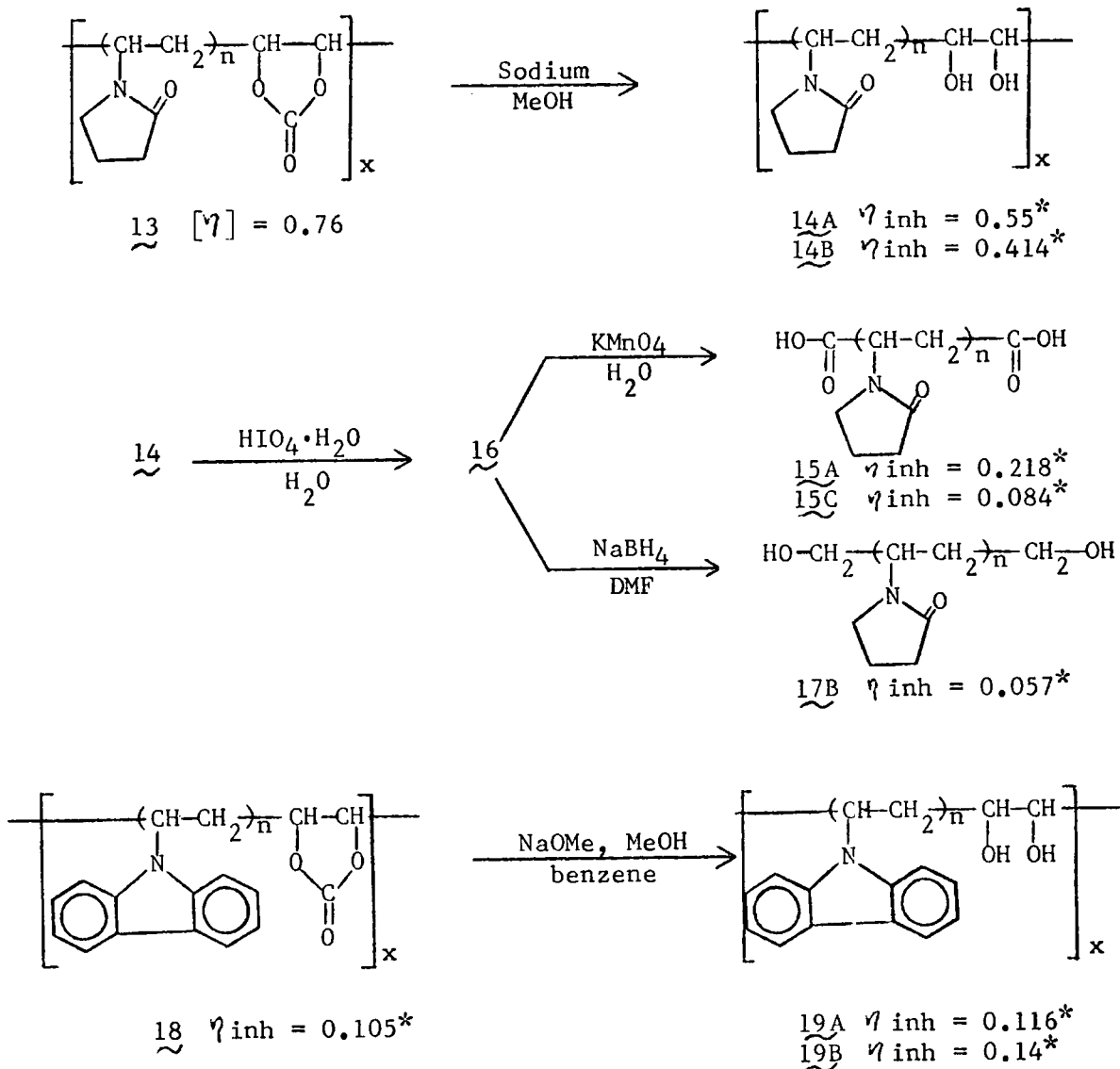
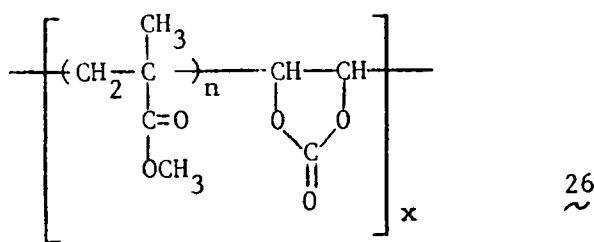


Figure 2. Preparation of polymers 13 through 25.

* Measured at a concentration of 0.5 g/dl and at 25°.

Poly(acenaphthylene-co-phenyl vinylene carbonate) (23) was hydrolyzed to the corresponding homopolymer (24) having vinylene glycol linkages. Polymer 24 was then cleaved and reduced to a polymer terminated with primary and secondary alcohol groups (25) (see Figure 2). Copolymer 23 was of a low, less than 20,000, molecular weight as evidenced by the $[\eta]$ 0.095 in benzene at 25°. Upon cleavage and reduction of 23 to alcohol endgroups, a slight viscosity increase was obtained, $[\eta]$ 0.128.

Poly(methyl methacrylate-co-vinylene carbonate), (26), was prepared by a procedure similar to that used for the copolymer of styrene and vinylene carbonate. The initial polymerization solution contained an excess of vinylene carbonate over methyl methacrylate and four times during the sixteen-day polymerization period, initiator and methyl methacrylate were added. The carbonate carbonyl band appeared at 1810 cm^{-1} in the ir spectrum of the copolymer which had $[\eta]$ 0.414 \bar{M}_v 110,000 (Fox et al. 1962).

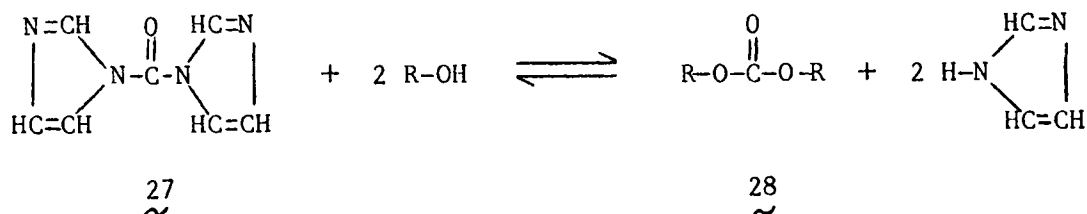


Treatment of 26 with 0.45 M sodium methoxide in tetrahydrofuran for four days caused the polymer to precipitate. The recovered polymer was insoluble in all of the usual solvents for poly(methyl methacrylate). The ir spectrum showed the absence of the carbonate carbonyl band so

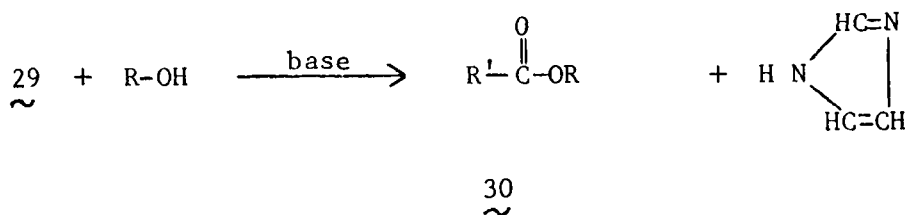
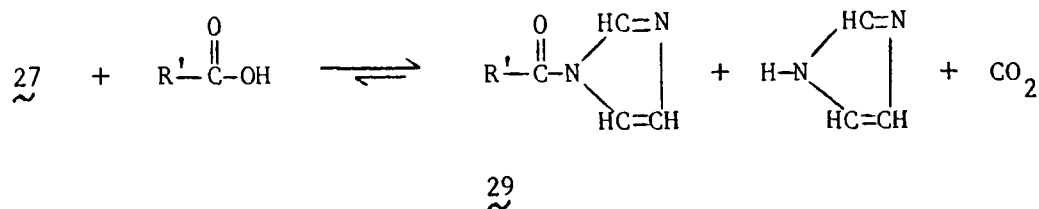
hydrolysis was essentially complete. Reducing the base concentration and reaction time resulted in incomplete hydrolysis of the carbonate and an insoluble polymer. Acid-catalyzed hydrolysis with *p*-toluene-sulfonic acid resulted in incomplete hydrolysis and a partially insoluble polymer.

It was proposed that the insolubility of the hydrolyzed copolymer from 26 was a result of cross-linking by transesterification between ester groups on one polymer chain with hydroxy groups on adjacent chains. A control experiment was carried out in which a mixture of pure poly(methyl methacrylate) and ethylene carbonate was treated with sodium methoxide in tetrahydrofuran under the same conditions as the copolymer. The recovered polymer was readily soluble in acetone, showing that no cross-linking occurred. This result does not rule out cross-linking by transesterification in the copolymer, as the pathway to cross-linking is much shorter in the copolymer than in a mixture of homopolymer and ethylene carbonate.

Carbonyl diimidazole (27) has been used as an activating group to prepare high molecular weight polyesters (Morgan 1965). It provides a pathway to esterification under extremely mild conditions. Carbonyl diimidazole (CDI) reacts reversibly with alcohols to form carbonates (28).

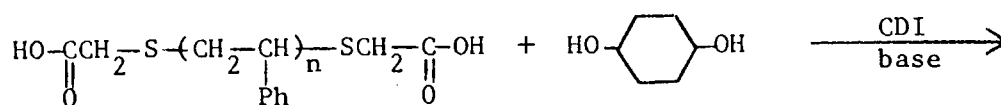


A trace of base catalyzes the esterification reaction; either the alkoxide of the alcohol to be esterified or a trace of sodium imidazolidine may be used. Carbonyl diimidazole reacts with a carboxylic acid to form an intermediate acid azolide (29). Since imidazole and carbon dioxide are formed the reaction is forced to the ester (30).

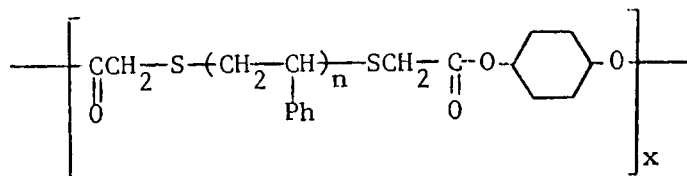


The feasibility of preparing block copolymers by a CDI-catalyzed esterification reaction was demonstrated by the chain extension of an acid-terminated polystyrene (12) with 1,4-cyclohexanediol and with an alcohol-terminated polystyrene (10) (see Figure 3).

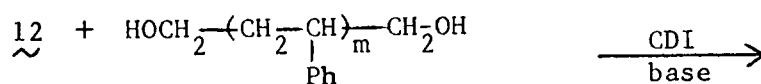
The copolymer 31 had $[\eta]$ 0.74. This viscosity increase corresponded to a 43% increase in molecular weight, from \bar{M}_v 123,000 to \bar{M}_v 176,000 calculated from $[\eta] = 1.13 \times 10^{-4} \bar{M}_v^{0.73}$ (Bawn et al. 1950). The plot of inherent viscosity versus concentration for copolymer 31 was strange in that it had a positive slope. Normally, extrapolation to infinite dilution results in $[\eta]$ being greater than η_{inh} ; however, in this case $\eta_{\text{inh}} = 0.95$ at 0.5 g/dl. Calculated at this point, $\bar{M}_v = 245,000$ for a 100% increase in molecular weight from 12. A molecular



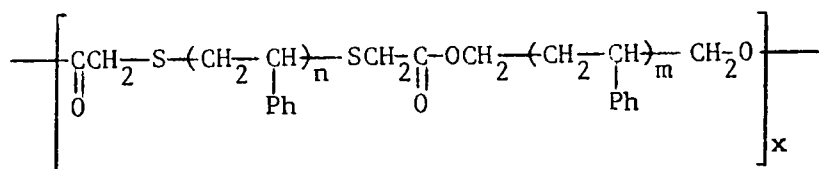
$$\sim \begin{matrix} [\eta] = 0.58 \\ \overline{M}_v = 123000 \end{matrix}$$



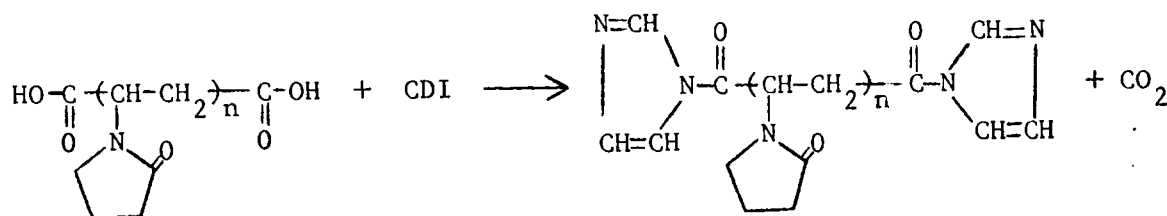
$$\sim \begin{matrix} [\eta] = 0.74 \\ \overline{M}_v = 176000 \end{matrix}$$



$$\sim \begin{matrix} [\eta] = 0.101 \\ \overline{M}_v = 13000 \end{matrix}$$



$$\sim \begin{matrix} [\eta] = 0.70 \\ \overline{M}_v = 158000 \end{matrix}$$



$$\sim \begin{matrix} [\eta]_{\text{inh}} = 0.084 \end{matrix}$$

$$\sim \begin{matrix} 33 \end{matrix}$$

Figure 3. Preparation of polymers ~ 31 through ~ 35 .

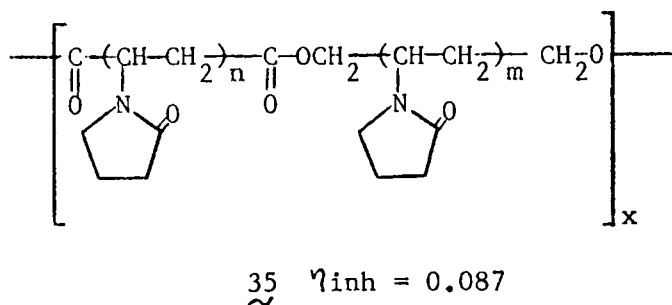
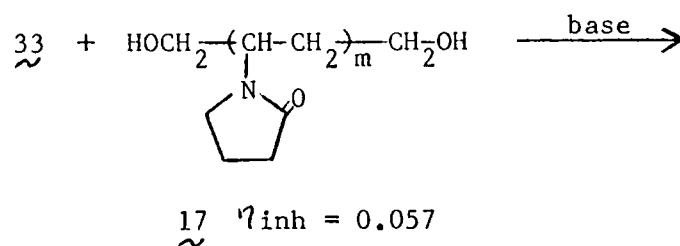
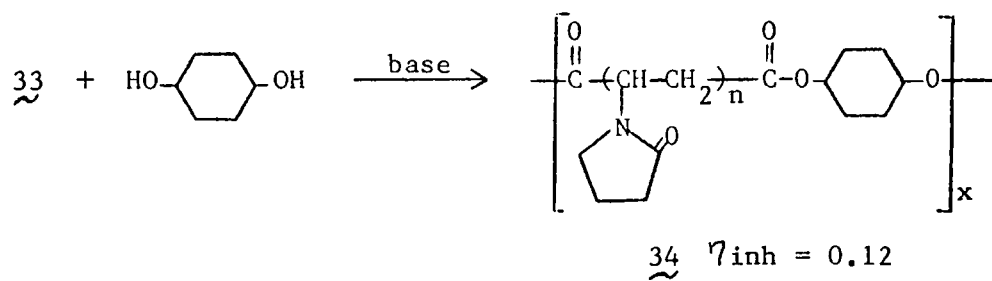


Figure 3.--Continued.

weight distribution study would have been helpful in determining the actual amount of coupling which did occur.

Copolymer 32, resulting from coupling acid-terminated polystyrene (12) with hydroxy-terminated polystyrene (10), had $[\eta]$ 0.70 for \bar{M}_v 158,000. This corresponded to a 41% increase in molecular weight from the average molecular weight of the starting polymers. As in the above case, the viscosity-concentration plot had a positive slope, $\eta_{inh} = 0.87$ at 0.5 g/dl.

Due to the large amount of absorbed water present in the polymers of N-vinyl pyrrolidone prepared in this investigation, a large excess of carbonyl diimidazole was necessary to cause esterification. Carbonyl diimidazole reacts preferentially and irreversibly with water, forming carbon dioxide and imidazole. Acid-terminated poly(N-vinyl pyrrolidone) (15) was reacted with an excess of CDI to give the intermediate acid azolide-terminated polymer (33) (see Figure 3). A sharp carbonyl band appeared in the ir spectrum of 33 at 1760 cm^{-1} where one was not evident in the spectrum of 15. The carboxyl carbonyl band was apparently overlapped with the large lactam carbonyl band.

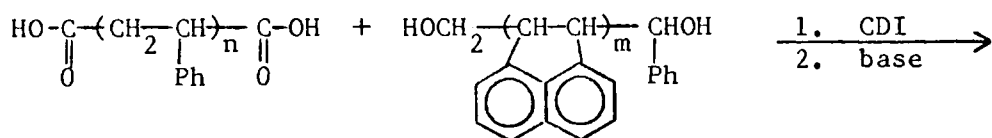
Polymer 33 was chain-extended with 1,4-cyclohexanediol to give copolymer 34 with a 42% increase in viscosity, from η_{inh} 0.084 for polymer 15 to η_{inh} 0.12 for polymer 34.

Similarly, 33 was coupled with hydroxy-terminated poly(N-vinyl pyrrolidone) (17) to give 35, η_{inh} 0.087 for a 38% increase in viscosity from the average of the starting polymers (see Figure 3).

Partial success was obtained when carbonyl diimidazole was used as the activating agent in esterifications between different homopolymers. Polystyrene with acid endgroups (11) was coupled to polyacenaphthylene with hydroxy endgroups (25) to give a polymer having a viscosity 9% greater than the mixture of starting polymers. Since there was 100% recovery of polymer, this viscosity increase indicated that a small amount of block copolymer (36) was formed (see Figure 4).

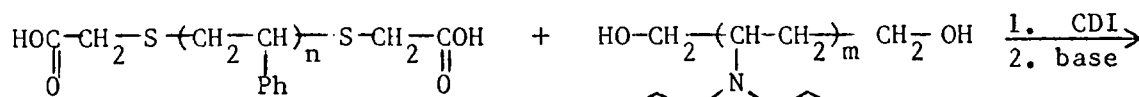
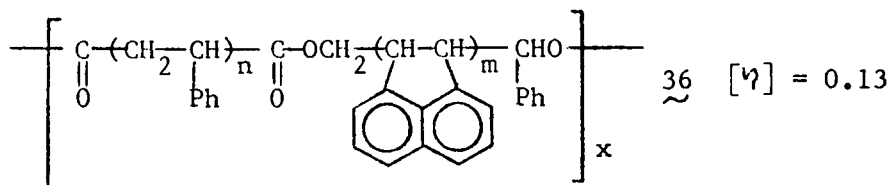
When polystyrene and poly(N-vinyl carbazole) were coupled using the CDI reaction (see Table 1), viscosity increases of 2.8% to 28% were recorded. These percents were calculated from the average viscosity of the starting materials as the solvent (benzene) was the same in all cases. The small increases are not significant since less than 100% of the polymer was recovered after reaction. One fact is obvious from examining Table 1--the greatest viscosity increase was obtained when polystyrene with acid endgroups (12) was used in the synthesis of block copolymer 37. This indicates that there are probably more reactive endgroups on the polymer prepared by chain transfer than on the acid-terminated polymers prepared by cleavage of the vinylene carbonate copolymer (see Figure 4).

In all phases of this investigation, the molecular weight distribution of the polymers would have been extremely valuable in assessing the extent and type of cleavage and coupling. In further work, endgroup analysis by one of the available methods is suggested. The general feasibility of this method of making block copolymers has been demonstrated, but much more study could be carried out along the lines mentioned above.



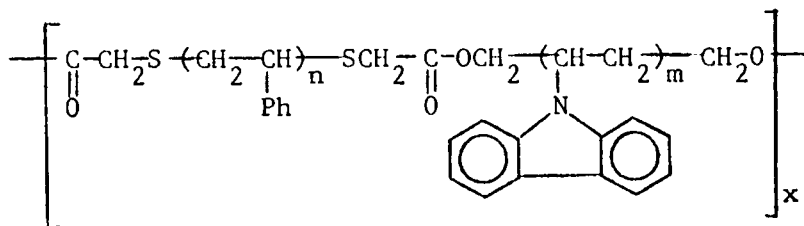
$$\underset{\sim}{11} \quad [\eta] = 0.101$$

$$\underset{\sim}{25} \quad [\eta] = 0.128$$



$$\underset{\sim}{12} \quad \eta_{\text{inh}} = 0.57$$

$$\underset{\sim}{21} \quad \eta_{\text{inh}} = 0.078$$



$$\underset{\sim}{37} \quad \eta_{\text{inh}} = 0.606$$

Figure 4. Preparation of polymers $\underset{\sim}{36}$ and $\underset{\sim}{37}$.

TABLE 1

POLY(STYRENE-b-N-VINYL CARBAZOLE) BY ESTERIFICATION

Attempt	Acid ^a	Alcohol ^a	Average Viscosity	CDI, mg ^b	Reaction Time		Percent Recovery	Viscosity ^c	Percent Viscosity Increase
					Before Base	After Base			
1	PS <u>12</u> 400 mg	PC <u>21</u> 100 mg	η_{inh} 0.472	25	17 hrs	24.5 hrs	100	η_{inh} 0.606	28.4
2	PC <u>20</u> 150 mg	PS <u>10B</u> 150 mg	$[\eta]$ 0.156	25	13	28	100	$[\eta]$ 0.176	12.8
3	PS <u>11A</u> 150 mg	PC <u>21</u> 100 mg	η_{inh} 0.092	130	23.5	22	83	η_{inh} 0.0945	2.8
4	PS <u>11A</u> 150 mg	PC <u>21</u> 100 mg	η_{inh} 0.092	65	No base used, refluxing toluene 24 hours		82	η_{inh} 0.095	3.3
5	PS <u>11A</u> 150 mg	PC <u>21</u> 80 mg	η_{inh} 0.093	80	12	17	85	η_{inh} 0.103	11.0

a. PS = polystyrene; PC = poly(N-vinyl carbazole).

b. CDI = carbonyl diimidazole.

c. η_{inh} measured at 0.5 g/dl.

EXPERIMENTAL

Materials

Styrene and N-vinyl-2-pyrrolidone (Matheson, Coleman, and Bell Co.) were purified by vacuum distillation. Acenaphthylene (J. T. Baker Chemical Co.) and N-vinyl carbazole (K. and K. Laboratories) were recrystallized prior to use. Benzene (Allied Chemical Co.) was distilled from sodium. Dimethylformamide was dried over anhydrous magnesium sulfate and then distilled from phosphorous pentaoxide. Dioxane was refluxed over sodium for 24 hours and then distilled.

Vinylene carbonate was prepared from ethylene carbonate (Matheson, Coleman, and Bell Co.) by the method of Johnson and Patton (1960) and purified by distillation from sodium borohydride. Phenyl vinylene carbonate was prepared by the method of Forgione (1968) from acetophenone (Matheson, Coleman, and Bell Co.) in a four-step synthesis.

Azobisisobutyronitrile (AIBN) (Matheson, Coleman, and Bell Co.), carbonyl diimidazole (Columbia Organic Chemicals), and 1,4-cyclohexanediol (Aldrich Chemical Co.) were used without further purification. The oxidizing agents, potassium permanganate (J. T. Baker Chemical Co.), and periodic acid (Matheson, Coleman, and Bell Co.), were used without purification as was the reducing agent, sodium borohydride (Matheson, Coleman, and Bell Co.).

Viscosities

The viscosities were measured at $25 \pm 0.1^\circ$. The flow times were recorded with a stopwatch and a range of 0.4 seconds per sample was accepted. The inherent viscosities, η_{inh} , are for a concentration of 0.5 g per 100 ml unless otherwise noted. The viscosities of polystyrene, polyacenaphthylene, and poly(N-vinyl carbazole) were measured in benzene and those of poly(N-vinyl pyrrolidone) were measured in distilled water.

Instrumental Analyses

All infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer from potassium bromide pellets unless specified as from a film. The polymer films were prepared by allowing a 10% solution of the polymer to dry on a metal gauze. The nuclear magnetic resonance spectra (NMR) were recorded on either a Varian Model HA-100 or a Varian Model A-60 spectrometer with tetramethylsilane as an internal standard.

Vinylene Carbonate

Chloroethylene carbonate was prepared by the method of Schaeffgen and Field (1966), starting with 220 g (2.5 moles) of ethylene carbonate in 200 g of carbon tetrachloride. An external ultraviolet light source (GE RS-type) was used instead of an internal source. Since the reaction time depends upon the rate of chlorine addition, a double Liebig condenser with ice water was used so the total reaction time was shortened to 3.5 hours. The most reliable indication of the end of the

reaction is the disappearance of two layers in the reaction flask. Ethylene carbonate is only partially soluble in carbon tetrachloride while mono-chloroethylene carbonate is completely miscible. After removal of the solvent under reduced pressure, the product was distilled at 7 mm. The lower boiling fraction (64-91°) consisting of polychlorinated products weighed 63.8 g, while the higher boiling fraction (91-103°) containing mono-chloroethylene carbonate and starting material weighed 244 g. A complete separation of these components with a 25 cm Vigreux column was not possible so the mixture was used in the next step of the synthesis.

Vinylene carbonate was prepared from the high boiling fraction from above by the thermal dehydrohalogenation method of Johnson and Patton (1960). The fraction to be pyrolyzed was dissolved in 100 ml of dry toluene and added dropwise to the column at the rate of approximately 2 ml per minute. Since a 30-cm heated column was used instead of the recommended 90-cm column, the temperature was raised 5° so that the column was maintained between 255 and 265°. Distillation of the pyrolyzate afforded vinylene carbonate (34.3 g) and unreacted starting material (75 g). Another 10.4 g of vinylene carbonate was obtained by repyrolyzing the recovered starting material. The technique of thermal dehydrohalogenation is much easier than the base-catalyzed method of Schaeffgen and Field, although the yield (20%) is lower. The product was confirmed by the strong strained ring carbonyl in the ir and by a singlet centered at 2.8 τ in the NMR spectrum.

Phenyl Vinylene Carbonate

Phenacyl acetate was prepared in 51% yield from acetophenone by the method of Ruggli and Knecht (1944), except that the product was purified by vacuum distillation instead of recrystallization as it tended to form an oil. Treatment of the acetate with barium carbonate in boiling water, according to Fischer and Busch (1891), gave phenacyl alcohol in 85% yield. Phosgene was condensed with phenacyl alcohol using the method of Forgiione (1968) to give phenyl vinylene carbonate in 39% yield. In order for this reaction to proceed satisfactorily, the reaction vessel was flame dried under nitrogen and the overall reaction time was increased several hours. The corrected melting point of 81-82° corresponded exactly to the literature value, and the product was confirmed by infrared and NMR spectra. Phenyl vinylene carbonate must be stored in the cold for it becomes yellow upon standing at room temperature.

Poly(styrene-co-vinylene carbonate) (7)

Freshly distilled styrene (3.4 g, 0.033 mol) and vinylene carbonate (8.6 g, 0.1 mol) were dissolved in 15 ml of benzene. After the addition of azobisisobutyronitrile (AIBN) (0.018 g, 0.108 mmole), the bottle and contents were flushed with dry nitrogen for 15 minutes. The bottle was sealed and placed in an oil bath at $60 \pm 2^\circ$. On the fourth and ninth days the bottle was charged with styrene (3.4 g) and AIBN (0.015 g). After a polymerization period of fourteen days, the copolymer was precipitated in methanol with about 4.0 g of calcium nitrate added to salt out the low molecular weight polymer. After two

reprecipitations, 7.5 g (40%) of a white polymer was obtained, $[\eta]$ 0.354 in benzene, \bar{M}_v 64,000 (Cantow et al. 1961). The ir spectrum (film) showed the carbonate carbonyl band at 1820 cm^{-1} overlapping an existing band in polystyrene.

Poly(styrene-co-vinylene glycol) From Tetrahydrofuran Solution (8A)

A solution of 3.0 g (7), sodium (0.6 g, 0.024 mol), 15 ml of methanol, and 75 ml of tetrahydrofuran was stirred at $35-40^\circ$ for 34 hours. Precipitation in methanol yielded 3.0 g for 100% recovery. The $[\eta]_{inh} = 0.308$ and the ir spectrum (film) showed the disappearance of the carbonate carbonyl band.

Poly(styrene-co-vinylene glycol) From Dioxane Solution (8B)

In an analogous manner to 8A a solution of (7) (3.5 g) in 50 ml of dioxane was treated with sodium (0.6 g, 0.024 mol) in 10 ml of methanol at room temperature for 3 days. The polymer was worked up as before for 100% recovery. The polymer was tan colored while the dioxane turned a dark orange. Benzene is a more satisfactory solvent for this reaction.

Polystyrene With Aldehyde Endgroups (9A)

A solution of periodic acid (1.5 g, 4.5 mmole) and 8A (1.5 g) in 30 ml of tetrahydrofuran was stirred for 3 days at room temperature. The polymer was worked up by precipitation into methanol to give an 80% yield, $[\eta]$ 0.101, \bar{M}_v 13,000 (Cantow et al. 1961). The aldehyde carbonyl appeared as a small sharp peak at 1710 cm^{-1} in the ir.

Polystyrene With Aldehyde Endgroups (9B)

The cleavage of 8A (1.0 g) with periodic acid (1.0 g, 3.0 mmole) in 20 ml of dioxane was attempted. After 9.5 hours the polymer had precipitated so the mixture was poured into methanol and the isolated polymer redissolved in 20 ml of tetrahydrofuran. Another 0.5 g of periodic acid was added and the reaction continued for 12 hours. Only 58% of the isolated polymer was soluble in benzene with $[\eta]$ 0.101. The remainder was an insoluble powder which was identical to polystyrene in the ir. Dioxane is not a good solvent for this oxidation.

Polystyrene With Hydroxy Endgroups (10A)

A solution of 212 mg of 9B in 15 ml of benzene was treated with sodium borohydride (0.2 g) for 48 hours at room temperature. The polystyrene was recovered in the usual way for 97% recovery. The hydroxyl groups were confirmed by the successful coupling of this polymer with an acid-terminated polystyrene.

Polystyrene With Hydroxy Endgroups (10B)

Poly(styrene-co-vinylene glycol) (8B, 1.5 g) was dissolved in 40 ml of tetrahydrofuran and periodic acid (1.0 g, 3.0 mmole) was added. After 60 hours the polymer was isolated by precipitation into methanol, dried, and redissolved in 40 ml of tetrahydrofuran. Sodium borohydride (1.0 g) was added and the mixture stirred for 68 hours. Precipitation in methanol gave 1.0 g of soluble polymer with $[\eta]$ 0.16,

\bar{M}_v 23,000, and 1.0 g of insoluble material resembling polystyrene in the ir.

Polystyrene With Acid Endgroups (11A)

Poly(styrene-co-vinylene glycol) (8A), 1.0 g, was dissolved in 75 ml of tetrahydrofuran and treated with periodic acid (1.0 g, 3.0 mmole) and potassium permanganate (1.0 g, 6.3 mmole). Distilled water (0.6 ml) was added to cause partial dissolution of the permanganate. After stirring for 6 days at room temperature, the polymer was precipitated in 4 N HCl and washed with 30 ml of methanol plus 10 ml of concentrated HCl and then with methanol, followed by drying in vacuo to give 60% of polymer, $[\eta]$ 0.12, \bar{M}_v 13,000. The ir spectrum was identical to polystyrene except for a small sharp peak at 1720 cm^{-1} .

Polystyrene With Acid Endgroups (11B)

As in the above case, 1.5 g of 8B was treated with the same amounts of the oxidizing agents in tetrahydrofuran, only this time the polymer was precipitated in methanol after 46 hours. About 2.0 g of calcium nitrate was added to the nonsolvent to salt out the low molecular weight polymer. Reprecipitation from benzene to methanol yielded 1.0 g for 66% recovery. The ir spectrum was as before and $[\eta] = 0.095$, \bar{M}_v 12,000.

Polystyrene With Acid Endgroups by Chain Transfer (12)

The chain transfer agent, dithiodiglycolic acid (2.5 g, 13.7 mmole), was dissolved in 20 ml of pyridine in an 8-oz wide mouth,

screw-cap bottle. Freshly distilled styrene (50 g, 0.48 mol) and AIBN (50 mg, 0.3 mmole) were added and the solution was flushed with dry nitrogen for 20 minutes. The bottle was sealed and placed in an oil bath at $50 \pm 2^\circ$ for 44 hours with occasional swirling. The polymer was worked up in the usual way to yield 8.0 g (16%) of a white polymer $[\eta]$ 0.58, \bar{M}_v 120,000, obtained from $[\eta]$ $1.13 \times 10^{-4} \bar{M}_v^{0.73}$ (Bawn et al. 1950).

Preparation of Poly(N-vinyl pyrrolidone-co-vinylene carbonate) (13)

A 2-oz wide mouth, screw-cap bottle was charged with freshly distilled N-vinyl pyrrolidone (33.9 g, 0.305 mol), vinylene carbonate (1.005 g, 11.7 mmole), and azobisisobutyronitrile (30.0 mg, 0.18 mmole). The bottle was flushed with dry nitrogen for 15 minutes, sealed, and placed in an oil bath at $60 \pm 2^\circ$ for 13.5 hours. The soft plug of clear polymer was dissolved in 100 ml of 1:1 acetone-methanol and precipitated in 500 ml of dry ether and reprecipitated twice. After drying, the weight was 16.1 g 46% conversion, $[\eta]$ 0.758. The ir spectrum (film) showed the carbonate carbonyl band at 1820 cm^{-1} .

Poly(N-vinyl pyrrolidone-co-vinylene glycol) (14A)

Poly(N-vinyl pyrrolidone-co-vinylene carbonate) (4.0 g, $[\eta]$ 0.758) was dissolved in 20 ml of methanol. A solution of sodium (1.0 g) in 25 ml of methanol was added and the solution stirred at room temperature for 4 days. The polymer was precipitated in dry ether and reprecipitated from methanol into ether twice to yield 2.9 g (72%), η_{inh}

0.55. The ir spectrum (film) showed the absence of the carbonate carbonyl band.

Poly(N-vinyl pyrrolidone-
co-vinylene glycol) (14B)

A solution of 13 (6.0 g) in 25 ml of methanol was treated with sodium (1.5 g) dissolved in 25 ml of methanol at 50° with stirring for 24 hours. After dilution with 50 ml of acetone, the polymer was precipitated in dry ether. Reprecipitation from water into acetone yielded 7.8 g. Poly(N-vinyl pyrrolidone) is very hygroscopic and three days in a vacuum oven at 72° removed only 0.6 g of water from the polymer. As a consequence of the adsorbed water, the $\eta_{inh} = 0.414$. The ir spectrum (film) showed a very pronounced OH stretching frequency and the absence of the carbonate carbonyl band.

Poly(N-vinyl pyrrolidone)
With Acid Endgroups (15A)

Poly(N-vinyl pyrrolidone-co-vinylene glycol) (0.75 g, η_{inh} 0.55) was dissolved in 25 ml of distilled water. Periodic acid (0.2 g, 0.6 mmole) and potassium permanganate (0.2 g, 1.3 mmole) were added and the solution was stirred at room temperature for 32 hours. The solution was filtered and the polymer precipitated in acetone and reprecipitated from methanol into dry ether to yield 0.35 g for 47% recovery. The η_{inh} was 0.218, indicating that cleavage occurred, although the acid carbonyl was not apparent in the ir.

Poly(N-vinyl pyrrolidone)
With Acid Endgroups (15B)

A solution of 14A (0.75 g) in 25 ml of pyridine and 2 ml of water was treated with periodic acid (0.2 g, 0.6 mmole) and potassium permanganate (0.2 g, 1.3 mmole). After stirring at room temperature for 41 hours, the solution was filtered and diluted with 25 ml of acetone. The polymer was precipitated in 300 ml of dry ether to yield 0.3 g for 40% recovery. This polymer was not characterized.

Poly(N-vinyl pyrrolidone)
With Acid Endgroups (15C)

Poly(N-vinyl pyrrolidone-co-vinylene glycol) (2.5 g, η_{inh} 0.414) was dissolved in 50 ml of distilled water, and periodic acid (1.0 g, 4.4 mmole) and potassium permanganate (1.0 g, 6.3 mmole) were added. After stirring at room temperature for 2 days, the polymer was precipitated in acetone and reprecipitated to yield 2.0 g (80%), η_{inh} 0.084.

Poly(N-vinyl pyrrolidone) With
Hydroxy Endgroups (17A)

To 25 ml of distilled water were added 0.5 g of 14A and periodic acid (0.2 g, 0.6 mmole). After stirring at room temperature for 14 days, the polymer was precipitated in acetone. After vacuum drying, the polymer was dissolved in 15 ml of dimethylformamide and treated with 0.5 g of sodium borohydride for 2 days at room temperature. After precipitation in acetone and vacuum drying, the weight was 1.0 g, indicating a large amount of adsorbed solvent. The ir spectrum showed a very broad OH stretching frequency.

Poly(N-vinyl pyrrolidone) With
Hydroxy Endgroups (17B)

Poly(N-vinyl pyrrolidone-co-vinylene glycol) (14B) (2.0 g, η_{inh} 0.414) was dissolved in 25 ml of dimethylformamide, and periodic acid (0.8 g, 2.4 mmole) was added. After stirring at room temperature for 3 days, sodium borohydride was added until no more hydrogen was evolved and then an additional 0.8 g of sodium borohydride was added. After a reduction time of 36 hours the polymer was precipitated in acetone for 100% recovery. The ir spectrum showed a very pronounced OH stretching frequency, η_{inh} 0.057.

Poly(N-vinyl carbazole-co-
vinylene carbonate) (18A)

N-vinyl carbazole (4.83 g, 25 mmole) was dissolved in 60 ml of chloroform, and vinylene carbonate (4.3 g, 0.05 mol) and AIBN (20 mg, 0.10 mmole) were added. The solution was degassed by two cycles of freeze-thaw and placed in an oil bath at $50 \pm 2^\circ$. On the second and fourth days the flask was charged with N-vinyl carbazole (4.8 g) and AIBN (20 mg and 15 mg), respectively. After six days the polymer was precipitated in methanol and reprecipitated four times from toluene into methanol. The polymer was yellow-orange and the yield was 2.0 g for 11% conversion. The ir spectrum showed the carbonate carbonyl at 1812 cm^{-1} .

Poly(N-vinyl carbazole-co-
vinylene carbonate) (18B)

N-vinyl carbazole (14.5 g, 75 mmole) was dissolved in 100 ml of benzene and recrystallized vinylene carbonate (4.3 g, 0.05 mol) and

AIBN (75 mg, 0.45 mmole) were added to the solution. After degassing by a freeze-thaw cycle, the flask was placed in an oil bath at $50 \pm 2^\circ$ under vacuum. After five days AIBN (35 mg) was added and the flask degassed and replaced in the oil bath for another nine days. Precipitating the polymer in methanol and reprecipitating from benzene into methanol yielded 8.5 g (45%) of a nearly white polymer unlike the above attempt, η_{inh} 0.105 (benzene). The ir spectrum showed the sharp carbonyl band at 1812 cm^{-1} , confirming the presence of vinylene carbonate.

Poly(N-vinyl carbazole-co-vinylene glycol) (19A)

To 3.0 g of 18B dissolved in 75 ml of dioxane was added 0.75 g of sodium dissolved in 15 ml of methanol. After stirring at room temperature for 3 days the polymer was precipitated in methanol and reprecipitated from benzene into methanol to yield 3.5 g of polymer, η_{inh} 0.116, after drying in a vacuum oven. There may have been adsorbed methanol since the OH stretching frequency in the ir was quite pronounced.

Poly(N-vinyl carbazole-co-vinylene glycol) (19B)

A solution of 18B (5.0 g) in 75 ml of benzene was treated with 0.8 g of sodium dissolved in 15 ml of methanol for 4 days at $40 \pm 2^\circ$. After precipitation and reprecipitation into methanol the yield was 4.4 g (88%), η_{inh} 0.14. The ir spectrum showed the absence of the carbonate carbonyl.

Poly(N-vinyl carbazole)
With Acid Endgroups (20)

Poly(N-vinyl carbazole-co-vinylene glycol) 19A (1.2 g, η_{inh} 0.116) was dissolved in 50 ml of benzene plus 25 ml of tetrahydrofuran. Periodic acid (0.8 g, 3.5 mmole), potassium permanganate (0.8 g, 5.0 mmole), and distilled water (0.6 ml) were added, and the mixture was stirred at room temperature for 4.5 days. The polymer was precipitated in methanol to yield 0.73 g for 61% recovery, $[\eta]$ 0.152.

Poly(N-vinyl carbazole) With
Hydroxy Endgroups (21)

A solution of 19A (1.2 g) and periodic acid (0.8 g) in 25 ml of tetrahydrofuran plus 10 ml of benzene was stirred at room temperature for 6 days. The aldehyde-terminated polymer was precipitated in methanol, dried, and redissolved in 25 ml of benzene plus 10 ml of dimethylformamide for treatment with sodium borohydride (1.0 g). After a reduction time of 36 hours, 0.78 g was recovered for 65%, $[\eta]$ 0.079.

Attempt to Prepare Poly(acenaph-
thylene-co-vinylene carbonate)

Recrystallized acenaphthylene (15.2 g, 0.1 mol), vinylene carbonate (1.0 g, 0.012 mol), and AIBN (50 mg, 0.3 mmole) were dissolved in 50 ml of benzene. The solution was degassed by two freeze-thaw cycles, and the flask was filled with nitrogen and placed in an oil bath at $50 \pm 2^\circ$. On the fifth, eighth, and tenth days, 50 mg of AIBN was added and the solution flushed with dry nitrogen. On the fourteenth day the solution was filtered to remove a white precipitate (0.5 g) and the polymer was precipitated in methanol to yield 6.4 g

(39%) of a yellow polymer. The ir spectrum of this polymer was identical to that of polyacenaphthylene, meaning that no copolymer was formed. The unidentified white precipitate showed both a carbonyl band at 1612 cm^{-1} and a broad OH stretching frequency in the ir.

Poly(acenaphthylene-co-phenyl vinylene carbonate) (23)

Recrystallized acenaphthylene (7.6 g, 50 mmole) and phenyl vinylene carbonate (0.8 g, 5 mmole) were dissolved in 35 ml of benzene. After the addition of AIBN (40 mg, 0.2 mmole) the solution was degassed by freeze-thaw and placed in an oil bath at $50 \pm 5^\circ$. On the fifth day AIBN (25 mg) was added under a stream of dry nitrogen and the polymerization was continued for three more days. Precipitation in methanol and two reprecipitations from benzene to methanol yielded 2.6 g (31%) of light orange polymer, $[\eta]$ 0.095, and the ir spectrum showed the carbonate carbonyl at 1815 cm^{-1} .

Poly(acenaphthylene-co-phenyl vinylene glycol) (24)

A solution of 23 (1.5 g) in 50 ml of benzene was treated with sodium (0.5 g) dissolved in 10 ml of methanol for 2 days at room temperature. The polymer was precipitated in methanol for 100% recovery, $[\eta]$ 0.115. The ir spectrum showed the absence of the carbonate carbonyl band.

Polyacenaphthylene With Hydroxy Endgroups (25)

A solution of 24 (1.0 g) in 20 ml of benzene plus 5 ml of dimethylformamide was stirred with periodic acid (1.0 g) for 42 hours at

room temperature. Sodium borohydride was added until no more hydrogen was evolved and then another 1.0 g was added along with 10 ml of benzene. After 3 days the polymer was precipitated in methanol for 100% recovery, $[\eta]$ 0.128.

Poly(methyl methacrylate-co-vinylene carbonate) (26)

Freshly distilled methyl methacrylate (3.0 g, 0.03 mol), vinylene carbonate (8.6 g, 0.1 mol), and AIBN (20 mg, 0.1 mmole) were dissolved in 15 ml of redistilled benzene in a 4-oz screw-cap bottle. Dry nitrogen was bubbled through the solution for 20 minutes and the bottle was sealed and placed in an oil bath at $60 \pm 2^\circ$. On the fourth, sixth, ninth, and thirteenth days, methyl methacrylate (3.0 g, 0.03 mol) was added along with AIBN (15, 15, 10, and 11 mg, respectively). The polymer solution was diluted with 50 ml of benzene and poured into excess methanol. The tan-colored polymer was reprecipitated twice from acetone into methanol and then vacuum dried. The dry weight was 11.7 (50%), $[\eta]$ 0.414, \bar{M}_v 110,000. A peak at 1810 cm^{-1} in the ir spectrum confirmed the presence of vinylene carbonate in the copolymer.

Attempts to Prepare Poly(methyl methacrylate-co-vinylene glycol)

A solution of 26 (3.0 g) in 75 ml of tetrahydrofuran was treated with sodium (1.0 g) dissolved in 20 ml of methanol for 4 days at room temperature. Much of the polymer precipitated after 3 days and the mixture was poured into excess methanol. The recovered polymer was insoluble in acetone, tetrahydrofuran, benzene, and dimethylformamide. The ir spectrum showed the absence of the carbonate carbonyl band.

Sodium (0.6 g) dissolved in 15 ml of methanol was used to treat 3.0 g of 26 in 75 ml of tetrahydrofuran for 2 days at room temperature. The recovered polymer was insoluble in acetone, although it did swell noticeably in the solvent. The carbonate carbonyl band was visible in the ir so hydrolysis was incomplete.

Treating 0.5 g of 26 dissolved in 25 ml of benzene plus 50 ml of acetone with p-toluenesulfonic acid (0.5 g) for 2 days at 50° resulted in a soluble polymer. The ir spectrum showed the carbonate band indicating incomplete hydrolysis. When the recovered polymer was treated with 1.5 g of p-toluenesulfonic acid in benzene-acetone for one day at 50°, a precipitate formed which did not redissolve in acetone. The ir spectrum showed that hydrolysis was incomplete.

Copolymerization of Acid-Terminated Polystyrene With 1,4-Cyclohexanediol (31)

To 1.0 g of 12 dissolved in 40 ml of tetrahydrofuran were added 1,4-cyclohexanediol (13.5 mg, 1.16×10^{-5} mol) and carbonyl diimidazole (CDI) (76 mg, 1.16×10^{-3} mol). After stirring at room temperature for 6 hours, the basic catalyst (0.2 ml of 0.5 g sodium in 10 ml of methanol) was added and the reaction continued for 14 hours. The polystyrene was precipitated in methanol for 100% recovery, $[\eta]$ 0.74, \bar{M}_v 176,000. The inherent viscosity-concentration plot had a large positive slope, η_{inh} 0.952 at 0.5 g/dl.

Coupling of Acid-Terminated Polystyrene
With Hydroxy-Terminated Polystyrene (32)

A solution of 12 (2.37 g [η] 0.58) and 10A (200 mg) in 40 ml of benzene was stirred at room temperature for 14 hours with CDI (44 mg, 2.7×10^{-4} mol). A trace of methoxide (0.4 ml of 0.25 g sodium in 13 ml of methanol) was added and the reaction continued for 18 hours. The polymer was precipitated in methanol for 100% recovery, [η] 0.70, \bar{M}_v 158,000. As in the above case, the viscosity plot had a positive slope with the η_{inh} at 0.5 g/dl being 0.87.

Poly(N-vinyl pyrrolidone) With
Acid Azolide Endgroups (33)

Poly(N-vinyl pyrrolidone) with acid endgroups (15C, 0.8 g) and an excess of CDI (0.5 g) were dissolved in 15 ml of dry dimethylformamide. After stirring for 25 hours, the polymer was recovered in anhydrous ether as a gummy coating in the beaker. After vacuum drying, the tough, horny plastic was chipped off of the beaker with difficulty. The ir spectrum showed a small carbonyl band at 1760 cm^{-1} which could be attributed to the acid azolide group or to excess CDI. Due to the instability of the endgroups, this polymer was used immediately in the following two copolymerizations.

Copolymerization of 33 With
1,4-Cyclohexanediol (34)

A solution of 33 (310 mg) and 1,4-cyclohexanediol (20 mg, 1.7×10^{-4} mol) in 10 ml of dry dimethylformamide was catalyzed by 0.4 ml of a solution of sodium imidazolide prepared by treating 60 mg of imidazole in 5 ml of dimethylformamide with excess sodium. After 46 hours

the polymer was precipitated in dry acetone for 75% recovery, η_{inh} 0.12 (in water). This corresponds to a 42% viscosity increase and indicates that the acid azolide intermediate actually was isolated.

Copolymerization of 33 With Hydroxy-Terminated Poly(N-vinyl pyrrolidone) (35)

To 200 mg of 33 and 200 mg of 17B (η_{inh} 0.057) dissolved in 10 ml of dry dimethylformamide was added 0.4 ml of the imidazolide solution prepared above. The polymer was precipitated in acetone for 55% recovery after 42 hours, η_{inh} 0.097.

Poly(styrene-b-acenaphthylene) (36)

Polystyrene with acid endgroups (11B, 100 mg), polyacenaphthylene with hydroxy endgroups (25, 60 mg), and CDI (60 mg, 1.85×10^{-4} mol) were dissolved in 15 ml of benzene plus 5 ml dimethylformamide. After stirring for 23 hours, 0.2 ml of an imidazolide solution prepared as above was added. In 4.5 hours, another 0.2 ml of imidazolide solution was added, and the solution was stirred for 25.5 hours. The polymer was precipitated in methanol for 100% recovery, $[\eta]$ 0.13.

Poly(styrene-b-N-vinyl carbazole)

The results of a series of attempts to prepare this block by the carbonyl diimidazole reaction are outlined in Table 1. While a viscosity increase was recorded in all cases, ranging from 2.8 to 28%, only two of the cases may be the result of coupling as less than 100% of the polymer was recovered in the other cases.

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