The Synthesis and Thermal Degradation of Some Diketone–Diamine Polymers

L. G. Kaufman, P. T. Funke, and A. A. Volpe[1]

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030. *Received August 19, 1969*

ABSTRACT: Polycondensation of several aliphatic and fluorine-containing, aromatic diamines with two isomeric aromatic diketones has been accomplished by means of acid-catalyzed solution polymerizations. The three polymeric products were semiaromatic or completely aromatic depending upon the diketone–diamine combination employed. Comparative thermal stabilities of the products both in air and in an inert atmosphere were investigated by thermogravimetric analysis. The completely aromatic, fluorine-containing polymers exhibited a high degree of thermal stability and all three of the polymers synthesized exhibited the surprising property of essentially the same resistance to initial thermal decomposition in the oxidative as well as the inert atmosphere. Three isomeric polymers synthesized in a previous investigation by the acid-catalyzed polycondensation of *m*-dibenzoylbenzene with the three phenylenediamines were subjected to thermogravimetric analysis after which the condensable volatiles were collected and then analyzed by combined vapor phase chromatography and mass spectroscopy. Separation and identification of the products given off upon thermal degradation by this combined analytical technique has indicated that different mechanisms are operative in the thermal decomposition of these isomeric polymers.

Polymeric Schiff bases synthesized from dialdehydes and aromatic diamines have been reported by several investigators to exhibit a high resistance to thermal stress.[2-5] However, there are very few examples reported in the literature in which a diketone is used as the starting dicarbonyl.[6,7] We have, therefore, undertaken to synthesize and characterize the thermal behavior of a series of polymers based upon the condensation polymerization of various aliphatic and aromatic diamines with several isomeric aromatic diketones. The polymers obtained varied in molecular structure since their backbones ranged from semiaromatic to completely aromatic depending upon the starting diketone–diamine combination employed.

Three polymers were synthesized by the acid-catalyzed polycondensation of *m*-dibenzoylbenzene with ethylenediamine, and by the polycondensation of *p*-dibenzoylbenzene with tetrafluoro-*m*-phenylenediamine and tetrafluoro-*p*-phenylenediamine. The thermal stability of these polymers was determined by thermogravimetric analysis in air and in an inert atmosphere. In addition, three isomeric polymers which were synthesized in a previous investigation[8] by the polycondensation of *m*-dibenzoylbenzene with *o*-, *m*-, and *p*-phenylenediamine were subjected to combined thermogravimetric analysis (tga)–vapor phase chromatography (vpc)–mass spectral analysis (ms). By means of this combined analysis, it was possible to degrade thermally a polymer sample, collect the condensable products given off upon thermal degradation, separate the products by vapor phase chromatography, and identify them by mass spectroscopy.

The general polycondensation reaction and the monomers employed in the course of this investigation are shown Scheme I.

Discussion

The polycondensation of *m*-dibenzoylbenzene with ethylenediamine and *o*-, *m*-, and *p*-phenylenediamine and the polycondensation of *p*-dibenzoylbenzene with tetrafluoro-*p*-phenylenediamine and tetrafluoro-*m*-phenylenediamine gave polymer products in 36–65% yield (Table I). Increased reaction times did not affect the yields of product obtained and all the polymers were highly colored, especially the completely aromatic systems.

Polycondensation of *m*-dibenzoylbenzene with ethylenediamine using an acid catalyst and xylene solvent yielded the semiaromatic polymer, poly(α,α'-diphenyl-*m*-xylylideneethylenediamine)[9] which was insoluble in common solvents. Thermogravimetric analysis of the system indicated a large weight loss beginning at 320° in nitrogen and at 300° in air (Figure 1). In nitrogen at 650°, polymer weight loss was approximately 65% and in air all of the sample was oxidized and volatilized at 610°.

The rather poor thermal stability of this system is not unexpected since its polymer backbone has a great deal of aliphatic character due to the presence of the ethylenediamine residue.

The two isomeric polymers, poly(α,α'-diphenyl-*p*-xylylidinetetrafluoro-*p*- and -*m*-phenylenediamine), synthesized by the polycondensation of *p*-dibenzoylbenzene

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(1) To whom correspondence should be addressed.

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(9) The method of naming this polymer as well as those subsequently discussed is consistent with the nomenclature of the polymeric Schiff bases found in the paper by G. F. D'Alelio, R. K. Schoenig, and J. V. Crivello, *J. Macromol. Sci.*, **A1**, 1299 (1967), and with the rules of nomenclature set forth in *Macromolecules*, **1**, 193 (1968).

SCHEME I

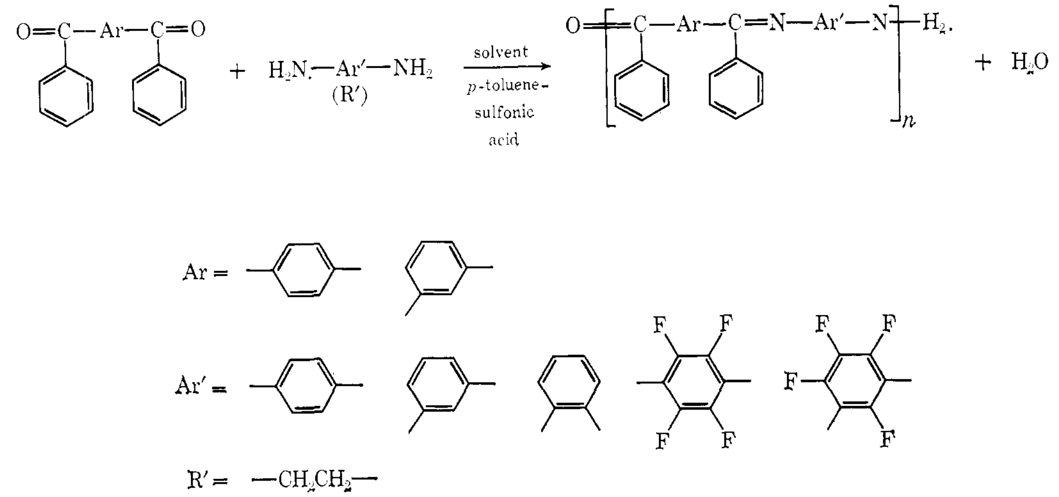
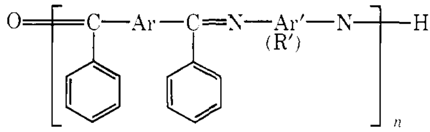


TABLE I
PRODUCTS OF POLYCONDENSATION OF DIKETONES WITH DIAMINES



Poly-mers	Ar-Ar′ (R′)	Yield, %	Mp, °C[a]	Crystallinity[b]	Calcd,[c] % C	Calcd,[c] % H	Calcd,[c] % N	Found, % C	Found, % H	Found, % N
I	*m*-Ethylene	36	235–238	Cryst	85.16	5.81	9.03	84.60	5.86	8.54
II	*p*-Tetrafluoro-*p*	52	295–298	Cryst	72.56	3.26	6.51	72.58	3.39	6.23
III	*p*-Tetrafluoro-*m*	52	220–223	Amorphous	72.56	3.26	6.51	72.81	3.22	6.23
IV	*m-p*	62	>300	Cryst	87.15	5.03	7.82	87.28	4.96	7.67
V	*m-m*	50	>300	Amorphous	86.28	5.09	7.74	86.54	5.26	7.31
VI	*m-o*	65	265–267	Cryst	87.15	5.03	7.82	87.22	5.19	7.63

[a] Uncorrected and taken by a capillary tube method. [b] The designations crystalline and amorphous are qualitative ones as obtained from powder X-ray diffraction patterns. Therefore, the systems may be undergoing glass transitions rather than melting. [c] Calculated values for systems in which the end groups are negligible, except for V which is calculated for a pentamer due to the presence of a substantial carbonyl absorption band which is not present in the infrared spectra of VI and to a very small extent in IV.

with tetrafluoro-*p*- and -*m*-phenylenediamine in decahydronaphthalene, were also insoluble in common solvents. They exhibited thermal stabilities which were similar to each other but much greater than the thermal stability of the semiaromatic polymer (Figures 2 and 3). These systems underwent less than 10% weight loss both in nitrogen and in air at just below 500°. Complete loss of sample in air took place at about 650° for both systems. In both cases, a remarkably large amount of residue (greater than 70%) was present in nitrogen at 800°. The residue was a shiny char which had the appearance of pyrolytic graphite and which had structural integrity as it did not crumble upon being touched.

Since these fluorinated polymers contain a completely conjugated backbone, a high resistance to thermal stress

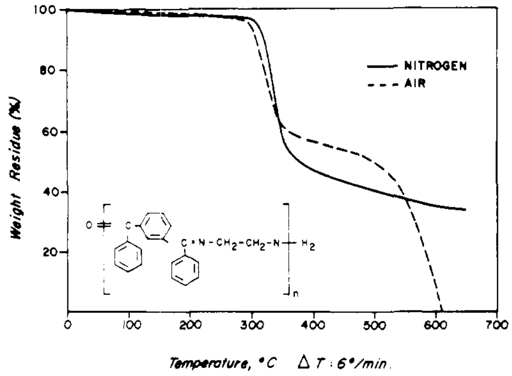


Figure 1. Thermogravimetric analysis of the *m*-dibenzoylbenzene–ethylenediamine system.

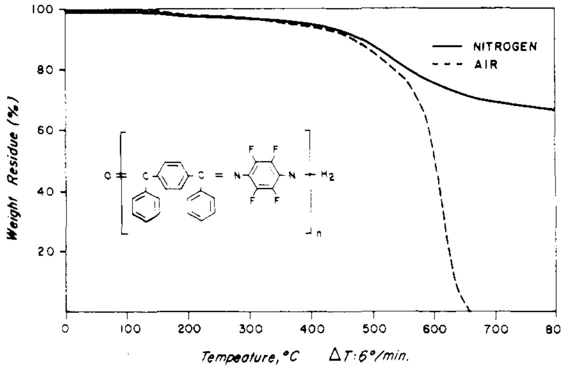


Figure 2. Thermogravimetric analysis of the *p*-dibenzoylbenzene–tetrafluoro-*p*-phenylenediamine system.

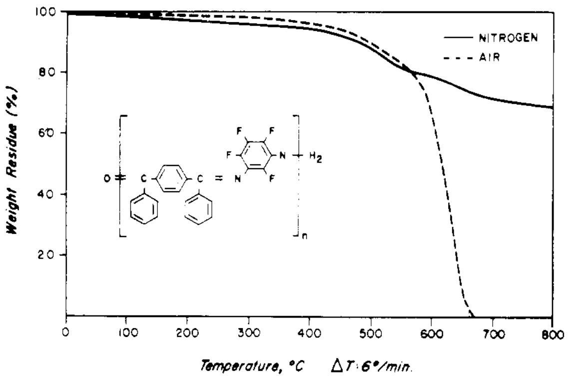


Figure 3. Thermogravimetric analysis of the *p*-dibenzoylbenzene–tetrafluoro-*m*-phenylenediamine system.

is not surprising. Also, substitution of CF bonds for some CH bonds also seems to increase thermal stability. Finally, the thermal stability of high temperature polymers is usually much greater in an inert atmosphere than in an oxidative one. However, these two polymers exhibit the unusual property of equally high resistance to initial thermal degradation both in air and in an inert atmosphere.

The polycondensation of *m*-dibenzoylbenzene with the three isomeric phenylenediamines has been outlined in detail in a previous publication.[8] Data obtained from thermogravimetric analysis of each of these three isomeric polymers are given in Table II.

The results from thermal analysis indicated that poly(α,α'-diphenyl-*m*-xylylidene-*o*-phenylenediamine) was less stable, both in an inert atmosphere and in air, than the other two isomers. In addition, the thermogram of poly(α,α'-diphenyl-*m*-xylylidene-*o*-phenylenediamine) exhibited two breaks in the slope of the curve whereas the other two isomers gave smooth thermograms with only one break in the curve. These observations indicate that a different mechanism of degradation from the other isomers may be operating in the case of the *meta–ortho* polymer.

Collection of the condensable volatiles given off upon thermogravimetric analysis and subsequent vapor phase chromatographic analysis and mass spectral analysis confirmed the results obtained from TGA alone. The major products isolated and identified upon thermal degradation of the *meta–para* and the *meta–meta* polymers were benzene, toluene, benzonitrile, and aniline along with somewhat lesser amounts of diphenylmethane. Minor products were biphenyl and *m*-benzyltoluene. The formation of all of these products may possibly take place as follows: benzene, pendant phenyl group cleavage with subsequent hydrogen atom abstraction from the residue; toluene, aniline, diphenylmethane, and *m*-benzyltoluene, main polymer chain fragmentation with subsequent hydrogen atom abstraction from the residue; benzonitrile, main polymer chain fragmentation; biphenyl, pendant phenyl group cleavage with subsequent free radical coupling of two phenyl groups.

Table II
Thermogravimetric Analysis of Polymers IV, V, and VI

Polymer	Dec pt,[a] °C (nitrogen)	Dec pt, °C (air)	% residue in nitrogen at 900°
IV (*meta–para*)	470	425	48
V (*meta–meta*)	475	475	52
VI (*meta–ortho*)	455	375	43

[a] The temperatures of decomposition correspond to the intersection of the slopes of the two lines of the individual thermograms according to the method of J. K. Stille, R. O. Rakutis, H. Mukamal, and F. W. Harris, *Macromolecules*, **1**, 431 (1968).

Elemental analysis of the polymer samples after thermal analysis indicated that both isomers yielded residues which had an increased carbon content and decreased hydrogen and nitrogen contents (see Experimental Section). These results are consistent with the relative amounts of degradation products formed.

Combined tga–vpc–ms analysis of the *meta–ortho* polymer gave markedly different results. The major products obtained were benzene and toluene with lesser amounts of diphenylmethane. The minor products were biphenyl, *m*-benzyltoluene, benzonitrile, and aniline. Elemental analysis of the residue after thermal analysis supported these observations since the carbon and hydrogen contents of the residue decreased whereas its nitrogen content increased. These results may indicate that the geometry of the *o*-phenylenediamine portion of the polymer is leading to cyclization and ultimate cross-linking of the residue, before nitrogen-containing fragments can be cleaved from the main polymer backbone.

Experimental Section

Comparative thermal stabilities of the polymer products were investigated in air and in either a nitrogen or helium atmosphere with a Du Pont 950 thermogravimetric analyzer programmed for a heating rate of 6°/min and with a gas flow rate of 40 ml/min. The initial sample weight in all cases was 20 mg. The infrared spectra of Nujol suspensions of the products were obtained with a Perkin-Elmer Infracord. The vapor phase chromatograph used was a Perkin-Elmer 900 model equipped with a 100-ft, 0.02-in. i.d. capillary column coated with Carbowax 20M. Mass spectral analysis was accomplished by means of a Hitachi Perkin-Elmer RMU-7 high-resolution mass spectrometer interfaced to the vapor phase chromatograph by means of a Biemann-Watson separator.[10] Crystallinity measurements were obtained with a General Electric XRD-6 diffractometer. Elemental analyses were performed by MHW Laboratories, Garden City, Mich.

Preparation of Poly(α,α'-diphenyl-*m*-xylylideneethylenediamine). To a mixture of 0.3 g (0.005 mol) of ethylenediamine and 0.05 g of *p*-toluenesulfonic acid monohydrate in 40 ml of dry xylene (mixture of isomers) was added 1.43 g (0.005 mol) of *m*-dibenzoylbenzene which was synthesized by the Friedel–Crafts acylation of benzene with isophthaloyl chloride.[8] The mixture was refluxed, with stirring, for 20 hr under a nitrogen atmosphere and the condenser was fitted with a Dean-Stark water trap. After the mixture was cooled, the solvent was removed by means of a rotary evaporator and an amorphous, tacky material was obtained. Upon the addition of 10 ml of 95% ethanol and 5 ml of chloroform and then heating upon a steam bath, a tan precipitate was obtained. After the precipitate was collected by filtration,

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[10] J. T. Watson and K. Biemann, *Anal. Chem.*, **36**, 1135 (1964).

repeatedly washed with a solution of equal volumes of hot 95% ethanol and chloroform, and then dried, 0.55 g (36% yield) of a light tan powder was obtained.

The infrared spectrum contained a C=N absorption band at 6.2 μ which was consistent with that expected of the desired product.[11] Elemental analyses and other data for this polymer as well as those subsequently discussed are given in Table I.

Preparation of Poly(α,α′-diphenyl-*p*-xylylidenetetrafluoro-*p*- and -*m*-phenylenediamine). A mixture of 0.715 g (0.0025 mol) of *p*-dibenzoylbenzene (synthesized by the Friedel-Crafts acylation of benzene with terephthaloyl chloride[8]), 0.45 g (0.0025 mol) of tetrafluoro-*p*- or -*m*-phenylenediamine (Whittaker Corp., San Diego, Calif.), and 0.05 g of *p*-toluenesulfonic acid monohydrate was refluxed, with stirring, in 40 ml of dry decahydronaphthalene under a nitrogen atmosphere for 20 hr. The condenser was fitted with a Dean-Stark water trap. After the mixture was cooled in an ice bath, a yellow precipitate separated out. The precipitate was collected by filtration and then Soxhlet extracted for 24 hr with a solution of equal volumes of 95% ethanol and water. After drying in an oven at 100° for several hours, 0.6 g (52% yield) of both products was obtained. The infrared spectra of both isomeric polymers exhibited C=N absorption bands at 6.2 μ.

Preparation of Polymers from *m*-Dibenzoylbenzene and *o*-, *m*-, and *p*-Phenylenediamine. The polycondensation reaction employed in the synthesis of these polymers has been outlined in detail in a previous publication.[8] Some of the properties of these systems along with other data are given in Table I.

Isolation and Identification of Condensable Products from Thermogravimetric Analysis. Volatile products given off upon thermogravimetric analysis in a helium atmosphere were condensed and collected by means of a liquid nitrogen trap. They were then dissolved in a few microliters of anhydrous ether and 1 μl of the solution was injected into a Perkin-Elmer 900 vapor phase chromatograph. The vapor phase chromatograph was temperature programmed to hold at 60° for 4 min, increase at 4°/min up to 200° and then hold at 200° indefinitely. The helium flow rate was maintained constant at less than 10 cc/min at the Biemann-Watson separator.

The Biemann-Watson separator allowed concentration of the compounds by removal of some of the helium carrier gas. They were then passed into an Hitachi Perkin-Elmer RMU-7 high-resolution mass spectrometer equipped with differential pumping to maintain a pressure of 10^{-6} Torr in the analyzer region. The mass spectra were obtained by rapid scan at a resolution of 700 and an electron energy of 70 eV.

Vapor phase chromatograms were obtained by monitoring a portion of the total ion current at the β slit of the mass spectrometer. The background current due to He^+ was compensated for by the zero setting of the electrometer and all other ions due to the various compounds were recorded to give the chromatogram.

One mass spectrum was obtained for each peak in the vapor phase chromatogram. All mass spectra were interpreted and then compared with spectra of a mixture of authentic samples. The mass spectra of the authentic samples as well as retention times of vapor phase chromatography were identical with those of the products given off upon thermogravimetric analysis.

Combined Analysis of Polymers by Tga-Vpc-Ms. A. Poly(α,α′-diphenyl-*m*-xylylidene-*p*-phenylenediamine). The condensable products, which were collected upon thermogravimetric analysis, were separated and identified by vapor phase chromatography, mass spectroscopy, and comparison with a mixture of authentic samples as described in the preceding section. The major products from the thermal degradation of the polymer synthesized from the *m*-diketone and the *p*-diamine were benzene, toluene, benzonitrile, and aniline. Minor products were biphenyl, diphenylmethane, and traces of *m*-benzyltoluene. This last compound was synthesized by means of a Friedel-Crafts alkylation of benzene with α-chloro-*m*-xylene. Its physical constants compared favorably with those reported in the literature.[12]

Elemental analysis of the polymer before thermal analysis and of the residue after thermal analysis yielded the results given in Table III.

TABLE III

	Found before thermal analysis, %	Found after thermal analysis, %	Δ
Carbon	87.28	90.30	+3.02
Hydrogen	4.96	3.36	−1.60
Nitrogen	7.67	5.76	−1.91

B. Poly(α,α′-diphenyl-*m*-xylylidene-*m*-phenylenediamine). The products obtained from thermogravimetric analysis of this polymer were collected, separated, identified, and confirmed in the manner described in the preceding section. Although elemental analysis indicated that the degree of polymerization of this system was only five, the same products as well as approximately the same relative amounts were obtained with this *meta-meta* pentamer as were obtained with the *meta-para* polymer. However, in addition to the major products (benzene, toluene, benzonitrile, aniline, and diphenylmethane) and minor products (biphenyl and *m*-benzyltoluene), small amounts of the two isomeric decahydronaphthalenes were also isolated and identified. Decahydronaphthalene was the solvent used in synthesizing all three isomeric polymers from *m*-dibenzoylbenzene and the three phenylenediamines. However, it was not present in sufficient amounts to affect elemental analysis.

TABLE IV

	Found before thermal analysis, %	Found after thermal analysis, %	Δ
Carbon	86.54	89.48	+2.94
Hydrogen	5.26	3.97	−1.29
Nitrogen	7.31	6.51	−0.80

TABLE V

	Found before thermal analysis, %	Found after thermal analysis, %	Δ
Carbon	87.22	86.76	−0.46
Hydrogen	5.19	4.55	−0.64
Nitrogen	7.63	8.69	+1.06

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(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958.

(12) J. H. Lamneck, Jr., and P. H. Wise, *J. Amer. Chem. Soc.*, 76, 1104 (1954).

Elemental analysis before and after thermal analysis gave the results shown in Table IV.

C. Poly(α,α'-diphenyl-*m*-xylylidene-*o*-phenylenediamine). Analysis of this system was carried out in the same manner as the preceding two. Although the products obtained from this system were the same as those obtained upon thermal degradation of the other two systems, the relative amounts were not the same. The major products were benzene and toluene with lesser amounts of diphenylmethane. Minor products were biphenyl, *m*-benzyltoluene, benzonitrile, and aniline. In addition, *cis*- and *trans*-decahydronaphthalene were also isolated and identified.

Elemental analysis before and after thermal analysis yielded the results given in Table V.

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Fractionation of Polymers by Thin Layer Chromatography. I. Separation

E. P. Otocka and M. Y. Hellman

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

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ABSTRACT: The separation of polymer fractions by thin layer chromatography (tlc) is described. Seven polystyrenes ranging from $\bar{M}_w = 10{,}300$ to 1,800,000 were successfully separated on either silica gel or alumina using mixed solvent elution or gradient elution techniques. Six polyethylene oxides ($\bar{M}_w = 1500$–$28{,}000$) were separated by simple mixed solvent elution on silica gel or by gradient elution on alumina. The ability of tlc to separate the polymer fractions appears to be based primarily on the relationship between adsorption and molecular weight.

Perhaps the most important characteristics of a given polymer sample are its molecular weight and polydispersity. Because of this, considerable effort is expended in the analysis and isolation of samples over a wide range of molecular weights and polydispersities.

Gradient elution and precipitation chromatography were the first column methods developed for both analytical and preparative fractionation of polymers. Both these techniques work by partitioning the polymer between a mobile solution phase and a supported stationary macroscopic condensed phase according to the solubility of a given molecular weight.[1,2] The role of adsorption in such fractionations has been discussed[3,4] but no definitive understanding has been reached.

In both analytical and preparative applications the solubility techniques are being supplanted by gel permeation chromatography (gpc). Fractionation in gpc is generally thought to occur *via* increasing exclusion of column volume with increasing hydrodynamic volume of polymer chains. Thus, the largest chains have the least column volume accessible to them, their flow is retarded least and they are eluted first.[5] Recently, an alternative explanation for elution order has been proposed by DiMarzio and Guttman.[6] In general, the conditions of gpc are designed to avoid adsorption.

The predictions of polymer adsorption theories and the observations of experiment indicate a strong influence of polymer molecular weight on both adsorption–desorption rates and the position of the adsorption equilibrium.[7–14] The amount of material adsorbed and the thickness of the adsorbed layer increase with molecular weight.[7,8,10,11] The rate of desorption decreases with molecular weight,[11,12] and strongly adsorbed macromolecules can displace previously deposited material that has less affinity for the substrate.[13,14]

Yeh and Frisch[15] attempted to use adsorption phenomena to fractionate polymers by a column technique. Fractionation was achieved, but flow rates were very low and in several cases the sample was not recovered quantitatively.

Thin layer chromatography (tlc) is a rapid technique

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(2) R. M. Screaton in "Newer Methods of Polymer Characterization," B. Ke, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, Chapter XI.

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