Macromolecules **1991,** *24,* 1962–1968

Cyclization and Copolymerization Behavior of *N*-Acryloyl-*N*′-phenylthiourea

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Received February 21, 1990; Revised Manuscript Received October 5, 1990

ABSTRACT: *N*-Acryloyl-*N*′-phenylthiourea (APTU) has been prepared and polymerized by a free-radical mechanism. The polymer formed has low molecular weight. This monomer is capable of polymerization in the solid state as evident from its DSC thermograms. It has also been found that APTU undergoes cyclization in solution. APTU was copolymerized with styrene (St), vinyl acetate (VA), acrylonitrile (AN), and methyl methacrylate (MMA). The reactivity ratios have been calculated in each case by several methods. From the four reactivity ratios a unique set of *Q*–*e* parameters has been calculated by a least-squares method. The thermal stability of the St–APTU and AN–APTU copolymers was found to decrease with increasing APTU contents.

Introduction

The synthesis of new polymer ligands has great practical and theoretical value.[1,2] The polymer–metal complexes could have catalytic activity[1,3] and offer excellent models for metalloenzymes.[1]

Thiourea and its derivatives are known to have numerous applications, including complexation with several metal cations.[4] They are used as corrosion inhibitors for steel and as antioxidant agents.[5] The antiirradiation characteristics of thiourea and its derivatives have also been reported.[6] Introducing a thiourea moiety as a pendant group to a polymer backbone could have several uses.

The free-radical polymerization of *N*-acryloyl-*N*′-phenylthiourea (APTU) leads to low molecular weight products, the mechanical characteristics of which are very poor.[7] The monomer must be copolymerized with another monomer to obtain copolymer including the desired group but having better mechanical properties. To prepare well-designed copolymers with tailored structures, precise monomer reactivity ratios must be determined.

This work describes the copolymerization of APTU with four monomers and evaluation of the reactivity ratios and the thermal properties of some of the resulting copolymers.

Experimental Section

APTU was prepared as previously described.[7] Monomer purification cannot be done by usual recrystallization since it undergoes cyclization upon heating. Purification was accomplished by reprecipitation from acetone into distilled water followed by filtration and drying under high vacuum at room temperature. The monomer can also be purified by dissolving in methanol followed by filtration and then cooling under mild suction. Yellow crystals separate out which may be quickly filtered and dried. All other monomers and solvents were purified by conventional techniques.

Copolymerization Procedure. The required amounts of monomer, solvent, and initiator (AIBN) were charged into glass vials stoppered with a rubber septum. Purified nitrogen gas was purged through a long needle into the cooled solution for several minutes, and the copolymerization was then conducted at 50 °C. For comparison, the copolymerization with styrene was conducted under high vacuum by using the freeze–thaw technique; although when the copolymerization was repeated according to the nitrogen method, no detectable differences were observed. Therefore, the latter method was adapted for the other systems. The copolymers were purified by repeated precipitation from acetone into methyl alcohol or petroleum ether and dried under vacuum at room temperature. The copolymers were analyzed for nitrogen and sulfur content at the Microanalytical Unit of Cairo University.

^{1}H and ^{13}C NMR spectra were measured with a Varian XL 200 spectrometer. The infrared spectra were obtained by using an FTIR 3 spectrometer (Nikon-Bunko Co., Tokyo, Japan). Viscosity measurements were carried out by using a Cannon–Ubbelohde-type viscometer in DMF as a solvent at 30 °C. Thermal analyses were performed both in air and under nitrogen at a heating rate of 10 °C/min. Thermogravimetry (TG) curves were obtained by using a DT-30B thermal analyzer equipped with sample container MDM-20. Differential thermal analysis (DTA) thermograms were obtained by means of a DA-30 Shimadzu Seisakusho Co. (Kyoto, Japan) thermal analyzer. A Perkin-Elmer DSC-7 was used to obtain the DSC thermograms of the APTU–St copolymers.

Results and Discussion

Homopolymerization and Cyclization Reactions. The monomer, APTU, undergoes free-radical polymerization using AIBN as initiator.[7] The rate of polymerization was followed dilatometrically as the volume decreased with the course of polymerization.[7] The polymer obtained in solution has a low molecular weight $[\eta] = 0.025$, even if the polymerization is conducted in the complete absence of oxygen by applying the high-vacuum freeze–thaw technique. GPC measurements of a polymer prepared in dioxane by using AIBN as initiator, gave $M_n = 2930$ and $M_w = 5309$. Typical ^{1}H and ^{13}C NMR spectra for the polymer PAPTU are given in Figure 1.

The polymer also polymerizes in the solid state without initiator as shown in the DSC thermograms in Figure 2. The first run (a) is the thermal behavior of the APTU sample before purification, while run b illustrates the behavior of the same monomer after reprecipitation from acetone solution into distilled water. The latter run shows the melting peak followed by an exothermic polymerization peak. On cooling, the measurements are repeated and a straight line (c) is obtained; i.e., the monomer has melted and polymerized to a material that does not melt up to 200 °C. The reason for obtaining low molecular weight polymer is due to the high chain transfer of the

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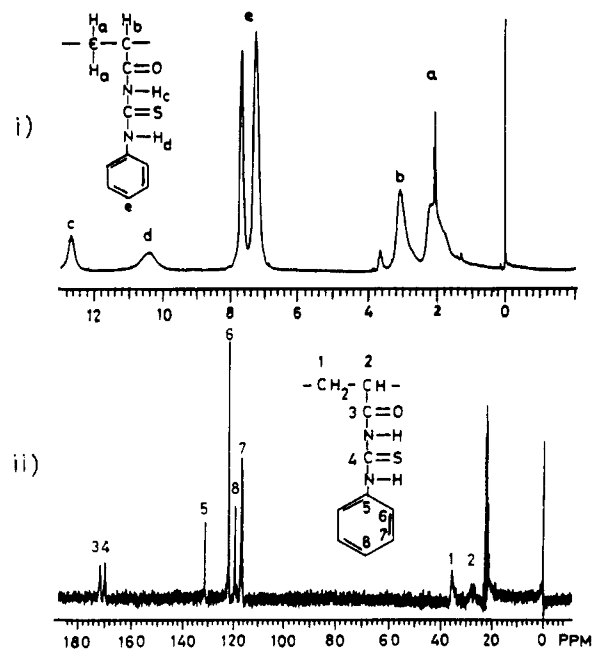


Figure 1. (i) ^{1}H NMR spectrum of PAPTU in acetone at room temperature. (ii) ^{13}C NMR spectrum of PAPTU in acetone at room temperature.

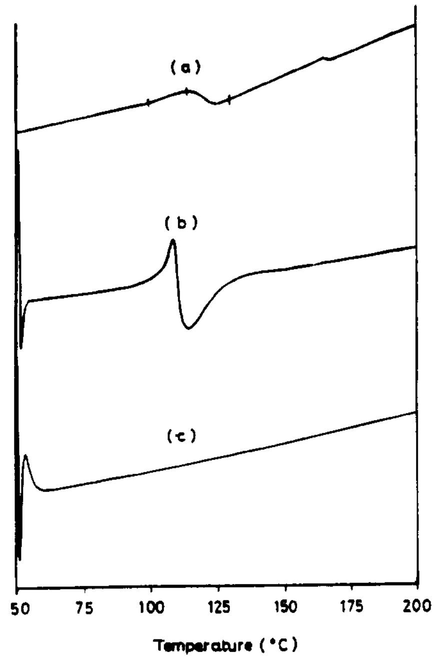
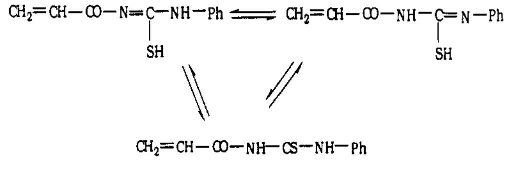


Figure 2. (a) DSC curve of unpurified APTU sample. (b) DSC curve of purified APTU sample. (c) Sample b after cooling and reheating.

free radical to the mercapto group according to the possible tautomerism:



$$CH_2{=}CH{-}CO{-}N{=}\underset{SH}{C}{-}NH{-}Ph \rightleftharpoons CH_2{=}CH{-}CO{-}NH{-}\underset{SH}{C}{=}N{-}Ph$$

$$CH_2{=}CH{-}CO{-}NH{-}CS{-}NH{-}Ph$$

On the other hand, it has been found that, on standing, the monomer undergoes cyclization in solution or even in the solid state at room temperature. The ability of APTU to act as a chain-transfer agent could be demonstrated by the following example: Methyl methacrylate (MMA) polymerizes in DMF at 70 °C with AIBN as initiator to give a polymer with a DP of 980. When 0.1 mol % APTU monomer is added, the polymer obtained has a DP of 580; on further increase of the APTU content to 2%, the DP drops to 230. In the meantime, the rate of polymerization was found to increase with increasing APTU content. The chain-transfer capacity of APTU was found to depend on the substitution of its phenyl group. Consequently, the molecular weight of substituted APTU is expected to change with the nature of the substituent. Indeed [η] of PAPTU changes from 0.025 for the unsubstituted to 0.14 for the *o*-cyano and 0.133 for the *o*-methoxy derivatives, respectively. Polymer prepared from the *p*-cyano derivative has much higher molecular weight [η] = 0.543 (polymerization was conducted in DMF at 65 °C for 14 h with AIBN).

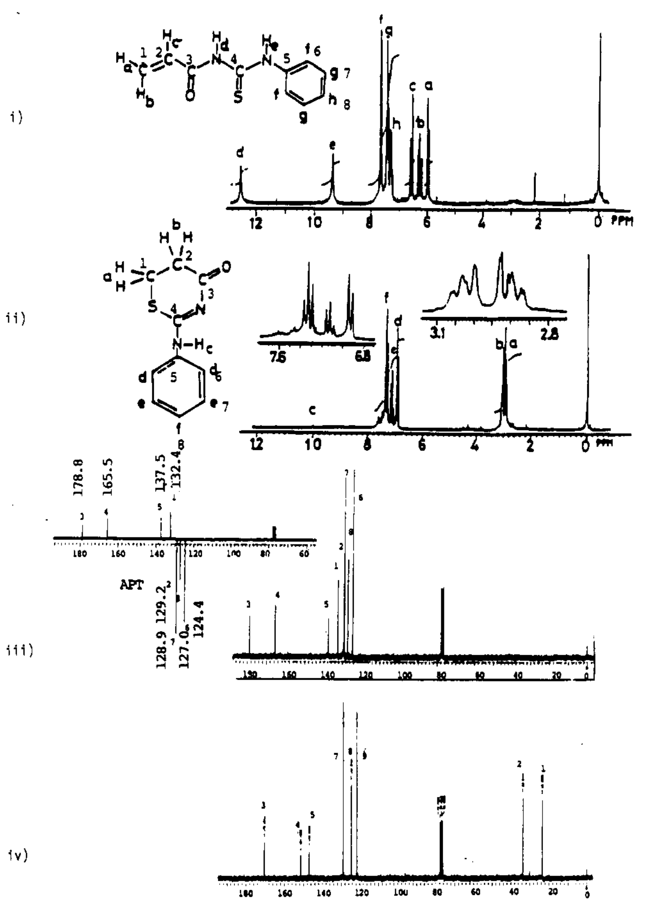
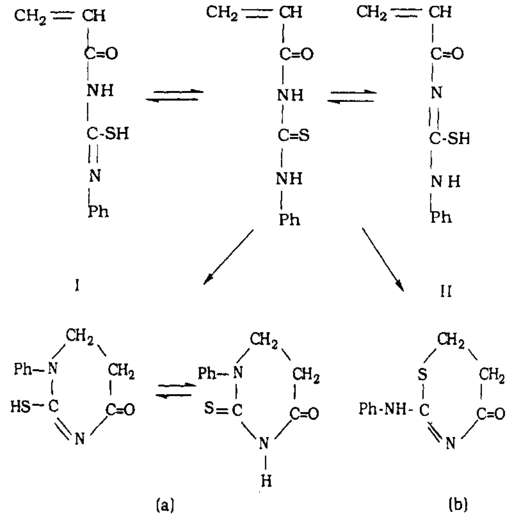


Figure 3. (i) ^{1}H NMR spectrum of APTU before cyclization. (ii) ^{1}H NMR spectrum of the cyclized APTU sample. (iii) ^{13}C NMR spectra of APTU before and (iv) after cyclization. Attached proton test (APT) shows the quaternary and CH$_2$s up and the CH and CH$_3$s down.

It has been found that at 50 °C, which is the polymerization temperature for APTU, the rate of polymerization is much faster than that of the cyclization. Therefore, we do obtain homopolymer and copolymers but of low molecular weights due to the chain-transfer reaction mentioned previously. The cyclization takes place most probably by the Michael addition of the SH group to the double bond, giving a compound that has the ^{1}H and ^{13}C NMR spectra shown in Figure 3. The cyclized compound was obtained by refluxing APTU in ethanol and traces of triethylamine for several hours followed by evaporation of the mother liquor to dryness under reduced pressure. The pure cyclized compound was then recrystallized from ethanol. Figure 3 also contains the corresponding spectra of the freshly prepared and purified APTU. After

Scheme I



complete cyclization, the vinyl protons disappear completely. The proton signal of the NH at 12.6 ppm disappears while that at 9.4 ppm shifts slightly downfield with reduction in intensity. A noticeable upfield shift of the two *o*-phenyl protons from 7.9 to 6.9 ppm can also be observed after cyclization. This latter shift is due to the effect of the lone pair of electrons of the nitrogen atom which is attracted toward the $-C{=}S$ group in the open structure but which on cyclization becomes more available to shield the ortho protons of the phenyl group, leading to this upfield shift. This shielding effect could also be seen in the ^{13}C NMR spectrum for the ortho, para, and quaternary carbon atoms. APT experiments were conducted to confirm further the proposed structure of APTU and its cyclized form. The rate of cyclization at different temperatures is measured in different solvents and will be published in a future paper.

The cyclization could proceed by either of the two possible pathways shown in Scheme I. Compound b is more probable based on its ^{13}C spectrum since the NCH_2 should have a signal at much lower field (40–80 ppm) than the observed shift (33.8 ppm) which is assigned to an SCH_2 structure.[8] Further evidence in support of this path (II) was obtained by using *N*-methylaniline instead of aniline in the reaction with the isothiocyanate derivative of acryloyl chloride. In this case, path I should be improbable and the resulting compound should be quite stable toward cyclization. On the contrary, the use of *N*-methylaniline gave exclusively the cyclized compound, the structure of which is shown in Figure 4. This means that the introduction of a methyl group onto the nitrogen of aniline facilitates the cyclization process enormously and confirms that the mercapto group is the one which participates in the addition.

PAPTU and its phenyl derivatives were found to form very stable complexes with several transition-metal cations. A detailed investigation of the chelating behavior of these polymers and their copolymers is underway. These complexes could have important biological or catalytic properties.

Copolymerization Behavior. Four comonomers were chosen for the copolymerization study with APTU to get a clear idea about its copolymerization behavior. Methyl methacrylate (MMA), styrene (St), acrylonitrile (AN), and vinyl acetate constitute a group of comonomers having a broad spectrum of values for their reactivities and polarities of the double bond[9] (the *Q*–*e* parameters) and should therefore exhibit different copolymerization behavior with the prepared APTU monomer.

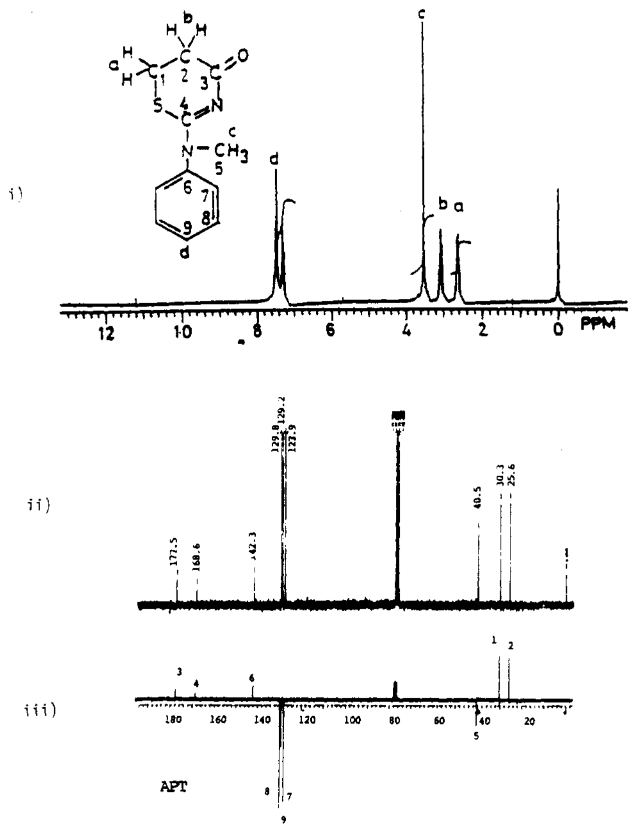


Figure 4. (i) ^1H NMR of 5,6-dihydro-2-methylanilino-(4*H*)-1,3-thiazin-4-one in acetone at room temperature. (ii) ^{13}C NMR of the same compound.

The copolymerizations were run to a low conversion for the four systems investigated. Each copolymer composition was calculated as the average value of four independent measurements: two from nitrogen and two from sulfur analyses. The monomer reactivity ratios were calculated in each case according to several methods: the linear Fineman–Ross,[10] the Kelen–Tudos,[11] the linear least-squares of Kelen–Tudos, and the nonlinear least-squares (NLLS)[12] methods, respectively. All calculations are based on the validity of the terminal model of copolymerization which was evident from the linearity of the Kelen–Tudos plots for the four systems as shown in Figure 5. The NLLS estimates of the reactivity ratios were used to construct theoretical copolymer composition curves and are plotted in Figure 6 together with the experimental points. A fairly good fit is observed. A summary of the methods used for the calculations is given in the Appendix.

Table I is a compilation of the reactivity ratios values obtained by the different methods. By surveying the data in Table I, one may observe that the values of the reactivity ratios obtained by the linear K–T method are in good agreement with those calculated by the NLLS method. One can also use eq A13 to compare the values of the parameter, α, obtained theoretically with that obtained experimentally as a guide in planning the copolymerization experiments. By doing so, it was found that a reasonable equality was obtained for the three systems MMA, VA, and AN. The theoretical value for α for the St system deviated appreciably from the experimental value. No apparent reason for this deviation is clear yet, and further investigations are required.

***Q*–*e* Scheme.** The *Q*–*e* scheme is an empirical one and has been subjected to many criticisms; however, many authors still prefer to calculate the *Q*–*e* values for newly prepared monomers. To obtain unique *Q*–*e* values, one

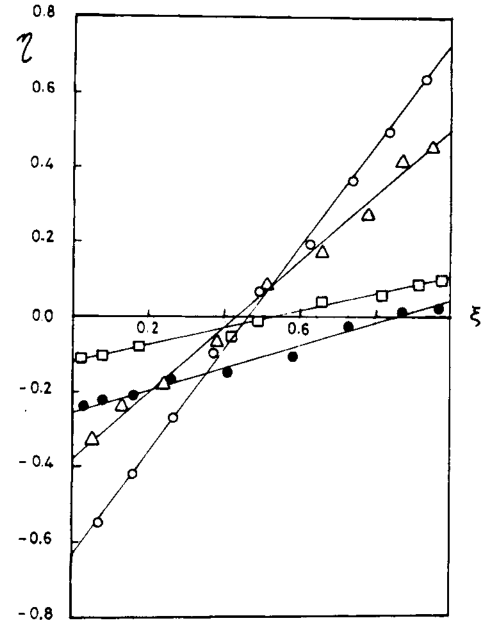


Figure 5. Kelen-Tudos plots for APTU with St (●), AN (△), VA (□), MMA (○).

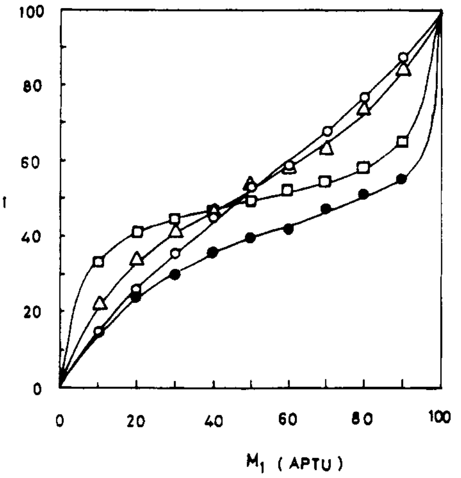


Figure 6. Copolymer composition diagram for the four systems. Points are experimental; curves are theoretical.

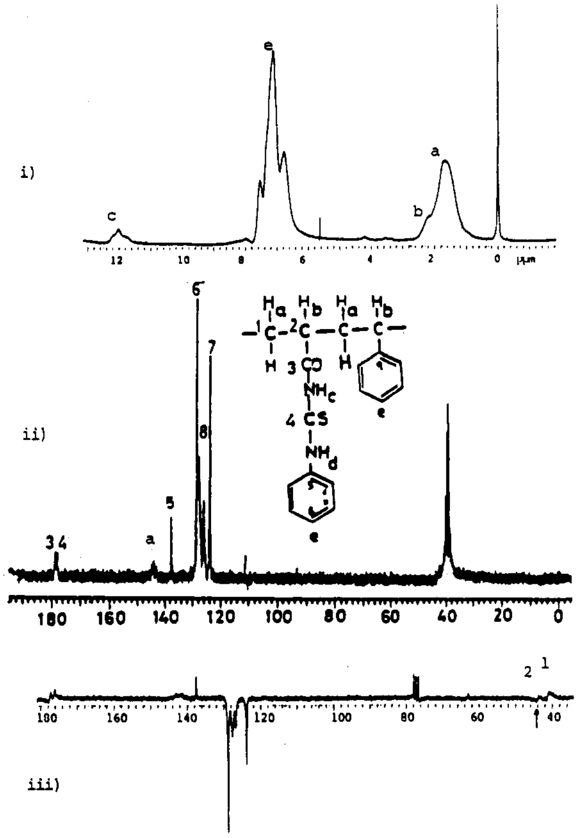


Figure 7. NMR spectra of St-APTU (70/30 mol %) copolymer: (i) ^{1}H, (ii) ^{13}C in DMSO at room temperature. (iii) APT to distinguish C1 and C2. (Solvent CDCl$_3$.)

Table I
Monomer Reactivity Ratios Calculated by Different Methods

	method	St	AN	VA	MMA
r_1	F-R	0.026	0.496	0.100	0.723
	K-T	0.032	0.486	0.102	0.714
	K-T(LLS)	0.032	0.405	0.108	0.714
	Δr_1	0.024	0.037	0.011	0.033
	NLLS	0.0303	0.480	0.100	0.675
r_2	F-R	0.514	0.306	0.118	0.588
	K-T	0.559	0.313	0.123	0.571
	K-T(LLS)	0.560	0.312	0.123	0.571
	Δr_2	0.048	0.031	0.011	0.030
	NLLS	0.560	0.310	0.123	0.564

has to use the copolymerization data of the given monomer with a variety of well-investigated monomers. The equation that relates the Q-e parameters with the reactivity ratios was given as[13]

$$r_1 = Q_1/Q_2 \exp - e_1(e_1 - e_2) \qquad (1)$$

which can be rewritten in the form

$$\ln Q_1/r_1 - e_1^2 = \ln Q_2 - e_1 e_2 \qquad (2)$$

By using the copolymerization data of several monomers with the required monomer and plotting the left-hand side of eq 2 vs e_1, which is the polarity of the reference monomers, one should obtain a straight line with a slope of e_2 and an intercept of ln Q_2.[13] In this way a unique set of the values of Q-e can be obtained instead of the two values usually obtained when the data of one copolymerization set are used. The application of this method to the present system using the four monomers gave quite scattered points with a very low correlation coefficient for the straight line. A much better fit was obtained by eliminating the VA data and using only the other three (St, MMA, and AN). By doing so, 0.81 and 0.49 were obtained for the Q and e parameters, respectively. The positive e value indicates that this monomer (APTU) has an electron-deficient double bond. This is reasonable since the copolymerization with St and VA, both having electron-rich double bonds, showed a stronger tendency for alternation than with AN and MMA.

Thermal Behavior of PAPTU and Its Copolymers. Thermal analysis is a powerful tool frequently used to evaluate the thermal stability of polymeric materials.[14] Spectra analysis (IR) could also be useful in following the thermal degradation of polymers. The latter method could also shed some light on the chemical changes accompanying the decomposition or the transformation of the polymeric material. To evaluate the effect of incorporation of APTU units into the copolymer chains, two copolymer sets were prepared with high conversion and were subjected to TGA and DTA analyses. Both St-APTU and AN-APTU copolymers were prepared by using the high vacuum technique. Table II contains some characteristics of these copolymers. Representative ^{1}H and ^{13}C NMR spectra of one of these copolymers are shown in Figure 7. Typical TGA thermograms for five St-APTU copolymers, in addition to PAPTU, are shown in Figure 8. As can be

Table II
High-Conversion APTU–St Copolymers Prepared in Dioxane at 50 °C

no.	APTU mol % M_1	conversion, %	S, %	N_2, %	m_1 (av)
1	7.8	36	5.70	4.80	22.18
2	27.0	52	8.03	7.16	35.54
3	45.0	62	9.56	8.35	44.65
4	59.0	65	10.05	8.88	48.41
5	80.0	42	11.67	10.32	60.08
6	100.0	30	15.50	13.59	100.00

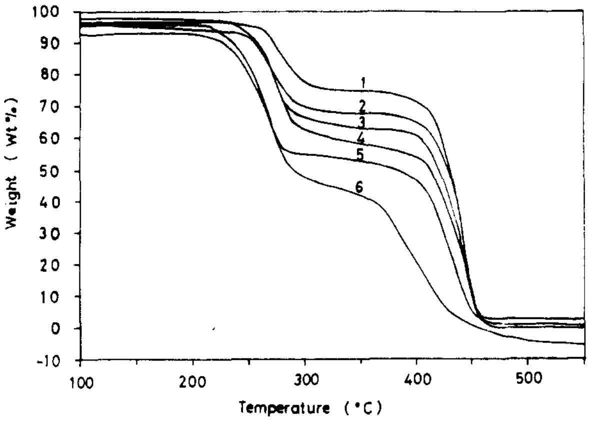


Figure 8. TG curves of St–APTU copolymers. St contents are given in Table II.

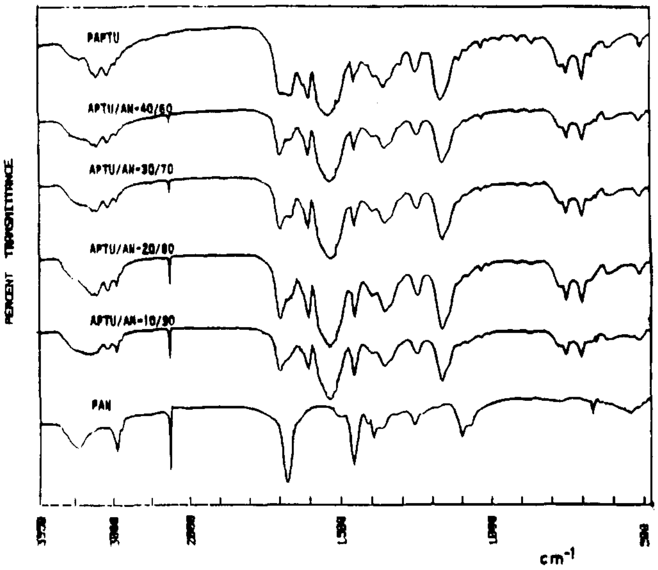


Figure 9. FTIR spectra of AN–APTU copolymers. The initial monomer compositions are indicated on the curves.

seen from the figure, the introduction of APTU units in the copolymer facilitates the decomposition process as evident from the increase of the percent decomposition with increasing APTU content.

In the case of the AN–APTU copolymers, FTIR spectroscopy has been used to follow the initial stage of decomposition. Figure 9 illustrates the IR spectra of the copolymers prepared, indicating their initial monomer feed ratios on the curves. Figure 10 illustrates the TG curves of this series. Again, the decrease of the thermal stability upon incorporation of APTU is evident. Upon analyzing the FTIR spectra of PAPTU and the AN copolymers, at different stages of decomposition, one can notice that the most pronounced effect in the IR spectrum is the appearance of a well-defined band at 2050 cm^{-1}, which increases in intensity with the course of thermal degradation. This band is undoubtedly due to the formation of the isothiocyanate group –N=C=S. The decomposition of the polymers starts then by the elimination of aniline. From Figures 8 and 10 it can be seen that the decomposition is always a two-stage process. The first stage probably corresponds to the elimination of aniline and/or a fragment of molecular weight around 135, which roughly corresponds to 65% of the APTU unit. Aniline (molecular weight 93) and the fragment of molecular weight 135, which could be PhN=C=S, were among the decomposition products in the mass spectra of APTU. On further heating of PAPTU and its copolymers to 800 °C, complete disintegration occurred and no residue remained, indicating main-chain scission and vaporization. It appears then that the incorporation of APTU units in the copolymers decreases their thermal stability. The DTA curves of PAN show the usual exothermic bands which correspond to the oligomerization reaction of the nitrile groups.[15] On the other hand, PAPTU shows an endothermic peak at 205 °C, which is an indication of polymer degradation and decomposition. The copolymers show intermediate behavior (in analogue to Figure 10). AN/APTU (90/10) has two small exothermic bands; the first starts at 220 °C followed by another at 263 °C. When the APTU content is increased to 40%, the exothermic peaks are reduced sharply and change into a series of small sharp peaks. This indicates that APTU prevents the oligomerization

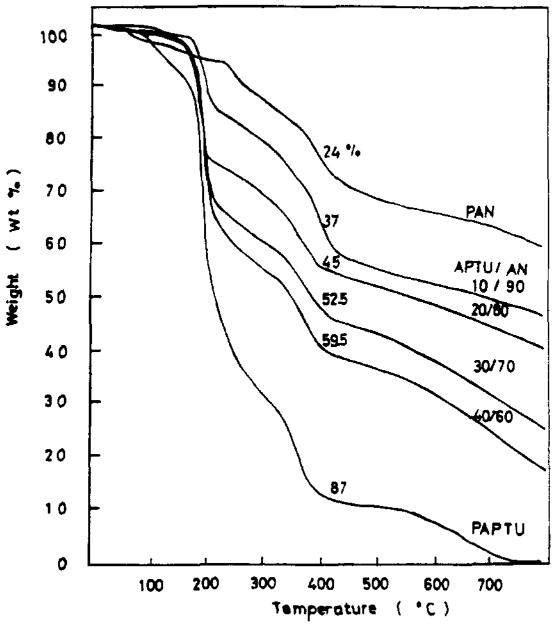
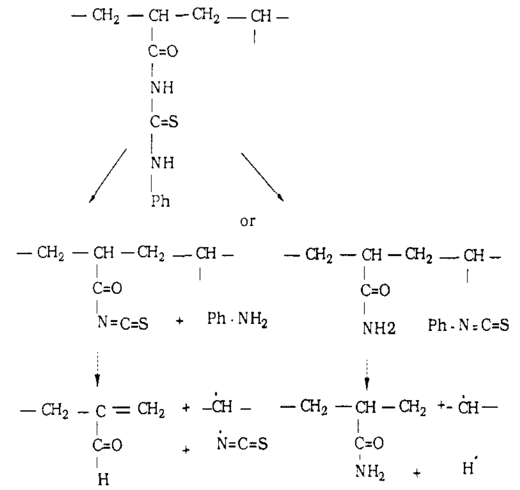


Figure 10. TG curves of AN–APTU copolymers.

Scheme II



reaction; in addition, it facilitates the process of decomposition. A possible mechanism for the thermal decomposition of PAPTU and some of its copolymers is outlined in Scheme II.

The free radicals formed would initiate main-chain scission, and this could accelerate the decomposition process and interfere with the nitrile cyclization step, thus preventing the oligomerization reaction in the case of the acrylonitrile copolymers.

Conclusion. A new monomer containing a thiourea derivative as a side group was prepared and copolymerized with four vinyl monomers. The reactivity ratios of the four systems were calculated. The Q and e parameters of the newly prepared monomer were obtained, and it was found that the monomer has an electron-deficient double bond. The polymer or the copolymers obtained from this monomer are well characterized by a low molecular weight due to high chain-transfer reaction of this monomer. The monomer also cyclizes upon heating in several solvents. The thermal stability of the prepared copolymers was found to decrease when the amount of the APTU in the copolymer was increased.

Acknowledgment. We are grateful to Professor G. B. Butler of the University of Florida for allowing the measurements of DSC and NMR spectra using the facilities of the University. We greatly appreciate the contribution of Professor Magdy Naoum of Cairo University in constructing the NLLS program.

Appendix

Fineman–Ross Method. This method is a linearization of the copolymer composition equation in the form[16]

$$r_2 = r_1(F - G) \text{ or } r_1 = r_2(1/F) + G/F \qquad \text{(A1)}$$

where G is defined as $x(y - 1)/y$ and F as x^2/y, where y is the mole ratio of monomers in the copolymer and x is the initial mole ratio in the monomer feed. The reactivity ratios can be then obtained as either slope or intercept or both.

Kelen–Tudos Method. Here the copolymer composition equation was linearized in the form

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha = r_1\xi - r_2/\alpha(1 - \xi) \qquad \text{(A2)}$$

where

$$\eta = G/(\alpha + F) \text{ and } \xi = F/(\alpha + F) \qquad \text{(A3)}$$

F and G have the same meanings as above. These two mentioned methods are applicable at low conversion.

Linear Least-Squares Kelen–Tudos Method.[17] In a later publication Tudos et al. have showed that the reactivity ratios may be determined by applying a linear least-squares method, i.e., by searching the minimum of the residual sum of squares:

$$S^2 = \sum[\eta_i - r_1\xi_i + (r_2/\alpha)(1 - \xi_i)]^2 \qquad \text{(A4)}$$

The solution of this linear problem is

$$r_1 = (1/D)[\sum\xi_i\eta_i\sum(1 - \xi_i)^2 - \sum\xi_i(1 - \xi_i)\sum(1 - \xi_i)\eta_i] \qquad \text{(A5a)}$$

$$r_2 = (\alpha/D)[\sum\xi_i\eta_i\sum\xi_i(1 - \xi_i) - \sum\xi_i^2\sum(1 - \xi_i)\eta_i] \qquad \text{(A5b)}$$

α is a parameter of symmetrization, the optimal value of which for a given series of measurements being

$$\alpha = (F_{\min}F_{\max})^{1/2} \qquad \text{(A6)}$$

i.e., the geometric mean of the lowest and highest values of F. D stands for

$$D = \sum\xi_i^2\sum(1 - \xi_i)^2 - [\sum\xi_i(1 - \xi_i)]^2 \qquad \text{(A7)}$$

The confidence of the estimated parameters can be calculated by using eqs A5a and A5b. The 100 β % confidence intervals are obtained by standard methods:[17,18]

$$\Delta r_1 = \pm t_\beta(n - 2)\left(\frac{S_{\min}{}^2}{n - 2}\frac{\sum(1 - \xi_i)^2}{D}\right)^{1/2} \qquad \text{(A8)}$$

$$\Delta r_2 = \pm\alpha t_\beta(n - 2)\left(\frac{S_{\min}{}^2}{n - 2}\frac{\sum\xi_i^2}{D}\right)^{1/2} \qquad \text{(A9)}$$

Expressions A8 and A9 are invariant to the reindexing of the monomers, and this means that the value of $S_{\min}{}^2$ changes upon reindexing: $S_{\min}{}^2(2,1) \rightarrow S_{\min}{}^2(1,2)$. Tudos and Kelen have shown that in a well-planned experiment it should be required that the r values obtained from the experimental data have approximately equal relative errors:[17]

$$\Delta r_1/r_1 = \Delta r_2/r_2 \qquad \text{(A10)}$$

From eqs A8 and A9 the expression

$$\Delta r_2 = \alpha\Delta r_1 \qquad \text{(A11)}$$

is obtained, which upon substitution into eq A10 gives

$$\Delta r_1/r_1 = \alpha\Delta r_1/r_2 \qquad \text{(A12)}$$

or

$$\alpha = r_2/r_1 \qquad \text{(A13)}$$

Consequently, a series of experiments is well planned if α experimentally calculated from the data (eq A6) equals the theoretical α values defined by eq A13.

Nonlinear Least-Squares Method. Behnken[19] and independently Tidwell and Mortimer have modified and extended the curve-fitting method. It consists basically of choosing initial estimates of r_1 and r_2 and a set of computations is performed that, on repetition, rapidly leads to a pair of values of the reactivity ratios which yields the minimum values of the sum of the squares of the differences between the observed and computed polymer composition. In this sense, the values obtained are unique since, for a given body of data, any person or set of persons following the calculation scheme will arrive at the same values of r_1 and r_2.

Let m_{2i} equal the observed mole fraction of M_2 in the polymer resulting from the ith experimental run, M_{2i} equal the initial mole fraction of M_2 used in the ith experiment, $r_1{}^j$ equal the jth estimate of r_1, $r_2{}^j$ equal the jth estimate of r_2, and $i = 1, 2, 3, ..., n$.

$$G_i^j = G(M_2; r_1{}^jr_2{}^j) = (r_2{}^jM_2{}^2 + M_2M_1)/(r_2{}^jM_2{}^2 + 2M_1M_2 + r_1{}^jM_1{}^2) \qquad \text{(A14)}$$

Approximately

$$m_{2i} = G_i^j + \left(\frac{\partial G_i^j}{\partial r_1}\right)(r_1{}^\circ - r_1{}^j) + \left(\frac{\partial G_i^j}{\partial r_2}\right)(r_2{}^\circ - r_2{}^j) + \epsilon_i \qquad \text{(A15)}$$

where ϵ_i is a random variable and r_1 and r_2 are the expectations of r_1^j and r_2^j, respectively. Then one computes the least-squares estimates of β_1 and β_2 for the equation[12]

$$d_i = m_{2i} - G_i^j = \beta_1\left(\frac{\partial G_i^j}{\partial r_1}\right) + \beta_2\left(\frac{\partial G_i^j}{\partial r_2}\right) + \epsilon_i \qquad \text{(A16)}$$

The least-squares estimates b_1 and b_2 of β_1 and β_2 provide corrections such that

$$r_1^{j+1} = r_1^j + b_1 \qquad r_2^{j+1} = r_2^j + b_2$$

should when substituted for r_1 and r_2 in eq A16 decrease the value of $\sum(d_i)^2$. Here

$$b_1 = \left[\sum d_i\left(\frac{\partial G}{\partial r_2}\right)\sum\left(\frac{\partial G}{\partial r_1}\right)\left(\frac{\partial G}{\partial r_2}\right) - \sum d_i\left(\frac{\partial G}{\partial r_1}\right)\sum\left(\frac{\partial G}{\partial r_2}\right)^2\right]/C$$

and

$$b_2 = \left[\sum d_i\left(\frac{\partial G}{\partial r_1}\right)\sum\left(\frac{\partial G}{\partial r_1}\right)\left(\frac{\partial G}{\partial r_2}\right) - \sum d_i\left(\frac{\partial G}{\partial r_2}\right)\sum\left(\frac{\partial G}{\partial r_1}\right)^2\right]/C$$

where

$$C = \left[\sum\left(\frac{\partial G}{\partial r_1}\right)\left(\frac{\partial G}{\partial r_2}\right)\right]^2 - \sum\left(\frac{\partial G}{\partial r_1}\right)^2\sum\left(\frac{\partial G}{\partial r_2}\right)^2$$

Values of $S_n = [\sum(d_i)^2]_n$ were obtained for

$$r_1 = r_1^j + [(n-1)/2]b_1$$

$$r_2 = r_2^j + [(n-1)/2]b_2$$

where $n = 1, 2, 3, ...$

Let

$$V = {}^1/_2 + (S_1 - S_3)/[4(S_1 - 2S_2 + S_3)] \qquad \text{(A17)}$$

Compute $S_4 = [\sum(d_i)^2]_4$ for $r_1 = r_1^j + Vb_1$ and $r_2 = r_2^j + Vb_2$. Then if $S_4 < S_1$, repeat the process by using in place of r_1^j and r_2^j the new estimates $r_1^{j+1} = r_1^j + Vb_1$ and $r_2^{j+1} = r_2^j + Vb_2$. If $S_4 > S_1$, V is reevaluated after b_1 and b_2 are halved. Three or four iterations were usually sufficient to get the desired values.

References and Notes

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Registry No. APTU, 17052-89-0; APTU (homopolymer), 124784-89-0; (APTU)(St) (copolymer), 132493-02-8; (APTU)(AN) (copolymer), 132493-03-9; St, 100-42-5; AN, 107-13-1; VA, 108-05-4; MMA, 80-62-6.