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Determination of Copolymer Composition Monomer Reactivity Ratios and Distribution Sequences of Different Acenaphthalene Copolymers Using the Ultra-Violet Absorption Method

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تعيين البوليميرات الأسنيفثالية التساهمية وتوزيعها التتابعي باستخدام طريقة إمتصاص الأشعة فوق البنفسجينة

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امتصاص الأشعة بواسطة الأنظمة البوليميرية المتصلة بوحدات أروماتية متدلية بالتفرع ينتج حالات مثارة ضوئياً. هذه الظاهرة جديرة بالاهتمام خاصة أن بعض نظام البوليميرات يمكن استخدامها في أنظمة تجميع ونقل الطاقة الشمسية.

تم تحضير بوليمر الاسنيفثالين بواسطة البلمرة بالمحلول عند 60° م. كما تم تحضير سلسلة من بوليمير الأسنيفثالين التساهمي مع الأكريلونيتريل والميثل أكريلونيتريل بواسطة البلمرة المستحلبية. وقد تم تعيين متوسط الوزن الجزئي اللزوجي يقع بين 18,000 و39,000 حسب نسب التركيز المختلفة لبوليمير الأسنيفثالين التساهمي، حيث تم تحضير تراكيز مختلفة من هذه البوليميرات (من 1-8) وتم تعيين امتصاصها لـ UV في التراكيز المختلفة على مدة طول موجي بين 250 إلى 350 نانوميتر وذلك باستخدام مطياف الأشعة فوق البنفسجية نوع كاري–14 وكذلك تم حساب نسبة تركيز الأسنيفثالين ونسبة فاعلية الوحدات في البوليمير التساهمي. حيث وجد أن مطياف الأشعة فوق البنفسجية يمكن استخدامه لتعيين تركيب البوليمير وكذلك التوزيع التسلسلي بطريقة مماثلة لطرق التحليل الفلزي ومعادلة التركيب البوليميري التساهمي. وبذلك تم تعيين متوسط أطول توالي السلاسل لبوليمير الأسنيفثالين التساهمي والتي وجد أنها متفقة مع الأطوال التي حسبت بمعادلة التركيب البوليميري التساهمي وهذا يوضح أن البوليمير التساهمي أسنيفثالين/اكريلونترايل مرتب على أساس تبادلي.

Abstract: *The absorption of radiation by polymeric systems containing pendent aromatic units produces photo-excited states. This phenomenon has generated considerable research interest since polymeric systems may be used for energy collection and transmission.*

Poly (Acenaphthalene) was prepared by solution polymerization at 60C^{0}. A series of copolymers of Acenaphthalene and acrylonitrile were prepared by emulsion polymerization. The molecular weights of homopolymer of Acenaphthalene and its copolymers were determined experimentally by viscosity measurements for different runs. The average molecular weight (Mv) was found to be between 18000 and 39000 depending on the copolymer composition ratios in the runs.

Different feed ratios of homopolymers and copolymers were prepared in different run numbers (1– 8). Cary 14 Ultra–Violet absorption spectrophotometer was used to determine the UV absorption of polymers with different concentration at wavelengths range between 250–350 nm. Then the percentages of Acenaphthalene (ACN) in the copolymer and monomer reactivity ratios were calculated.

It was found that Ultra-Violet absorption spectroscopy can be applied to give similar results

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for the copolymer percentage composition and distribution sequences consistent with elemental analysis and copolymer composition equation. The average lengths of a given sequence has been calculated and the sequence length of ACN units in the copolymer are in close agreement with those obtained using the copolymer composition equation, indicating the highly alternating character of the copolymer Ploy (ACN-CO-AN).

INTRODUCTION

The absorption of UV energy by fluorophores attached to a polymer chain and the subsequent energy migration by way of excitons are subjects of theoretical interest [1-2]. This phenomenon has general considerable research interest since polymeric systems may be used for solar energy collection and transmission. The production of these electronically excited states in polymeric systems and the photophysical behavior associated with those states continue to be an active area of research[3-4]. The preparation of polyacenaphthalene Poly (ACN) and its copolymers with 2-vinylnaphthalene (2VN) Poly (ACN-CO-2VN), acrylonitrile (AN) Poly(ACN-CO-AN), methacrylonitrile (MAN) Poly(ACN-CO-MAN), vinylcarbazol (VC) Poly (ACN-CO-VC), and the studies of the Exciton migration on these copolymers using excited singlets, excimers or exciplexes which is limited by polymer structure were previously reported [5-6].

The overall efficiency of excimer formation will be determined by polymer chain conformation. A helical conformation allows stacking of chromophores outside the main coil of the copolymer. Thus, intramolecular association depends upon the repeated distance between the *trans* groups of the helix.

Ultra-violet absorption spectroscopy (UV) as a tool for the determination of Monomer reactivity ratios (r_1 & r_2) as well as the distribution sequences of copolymer.

Determination of the copolymer composition and knowing the monomer reactivity ratio is very important for knowing and determining the longest energy migration lengths.

The maximum energy migration lengths in copolymers of Acenaphthalene with acrylonitrile, methacrylonitriles, and 1-vinylnaphthalene with the percentages (47%, 5%, 78%) of ACN in each of the copolymer were reported to be 70, 88 and 94 angstrom respectively [7].

The percentage of Acenaphthalene (ACN) in the copolymers was determined by different methods. In this work Ultra-Violet absorption spectroscopy was applied to give good results which are similar to those obtained by the tedious process of elemental analysis. This accurate and easily-handled technique was developed for poly(ACN-CO-AN) and poly(ACN-CO-MAN) as shown in Tables 1 and 2.

Another important techniques is the determination of the degree of alteration by knowing monomer reactivity ratios runs r_1 and r_2. It is also possible to determine the distribution sequences of the copolymers chain in a quantitative manner.

This sequence distribution can be determined and calculated by Harrowed and Ritchey equation[8] based on the run number (R) which is defined as "the average number of uninterrupted monomer sequences for runs that occur in a copolymer chain per 100 monomer units".

MATERIAL AND EXPERIMENTAL METHODS

Poly(Acenaphthalene) was prepared by solution polymerization at 60C^0 using Azo-bis-isobutyronitrile (AIBN) as an initiator in dry degassed benzene. Copolymers of Acenaphthalene and acrylonitrile were prepared by emulsion polymerization. [9], in a mixture of water/ethanol, potassium persulfate was used as an initiator. Emulsifier and surfactant were added.

The molecular weights of homopolymer of Acenaphthalene and its copolymer were determined experimentally by viscosity measurements for different runs by Ostwald viscosity method at constant temperature for all runs, then the Mark Sakurada equation { $[\eta] = k M^a$} was used. Where $[\eta]$ is the intrinsic viscosity, (k) and (a) are constants which depend on the solvent. (k) = 3.0×10^{-4} and (a) = 0.594 for benzene used as a solvent [10]. The number average molecular weight was found to be between 18000 and 39000 according to the copolymer composition ratios in the runs.

Samples of homopolymer and copolymers of Acenaphthalene were purified by dissolving the polymers in 100-ml benzene and precipitated by 600 cm ^{3} methanol. Drying was carried out in a vacuum at 25 C^o. 0.1 g/l of each of the polymer and copolymers were dissolved in 1,2-dichloroethane and the following three concentrations were prepared 2×10^{-3} g/l, 4×10^{-3} g/l, and 8×10^{-3} g/l.

Different feed ratios of homopolymers and copolymers were prepared in different run numbers (1 – 8).

Cary 14 Ultra – Violet absorption spectrometry was used to determine the absorption of polymers with different concentration at wavelengths between 250 – 350 nm.

RESULTS AND DISCUSSION

The UV absorption spectra for different concentrations of the homopolymer Acenaphthalene in 1,2-dichloroethane solvent and its copolymer Poly(ACN-CO-AN), were shown in spectra figures 1 and 2 respectively.

The percentage of ACN $[F_1]$ in the copolymers was determined from UV absorption spectra. The absorption at 290, 300 and 306 nm were used to calculate the percentage of ACN in the copolymers. At 290 nm, Poly (ACN) has a strong absorption peak. For a concentration of 8×10^{-3} g/l the absorbance is 0.43 as shown in figure 1.

The percentage composition of ACN in the copolymer is given by the following equation :

$$F = \frac{A_{copoly} \, g/l}{A_{homo.} \, g/l} \times 100 \qquad (1)$$

Where F is the percentage of ACN.

$A_{copoly.}$ is the absorption at concentration 6×10^{-3} g/l for the copolymer.

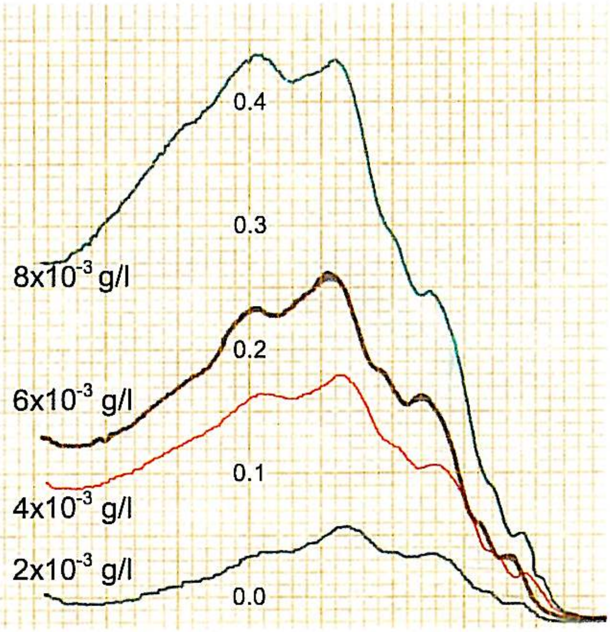

Fig. 1. UV spectrum of Poly(acenaphthalene) dissolved in 1, 2-dichloroethane at different concentrations, g/l. in, Abs 1.

A_{homo} is the absorbance at the same concentration for the homopolymer at a given wavelength.

Example :

run number 1:

$$F_1 = \frac{0.10}{0.26} \times 100 = 38.5\ \% \text{ at } \lambda\ 290 \text{ nm}$$

$$F_2 = \frac{0.65}{0.18} \times 100 = 36\% \text{ at } \lambda\ 300 \text{ nm}$$

The values in the denominator are obtained from figure 2.

These F values are listed in Tables 1 and 2.

The absorption at 290, 300, 306 nm. *vs.*concentrations of Poly (ACN) homopolymer plotted in figure 3 shows a maximum absorption at 290 nm.

The resulting values listed in Table 1 column (a) are the percentage of Acenaphthalene (F) in the copolymer Poly(ACN-CO-AN) calculated from experimental data of the UV absorption method. The

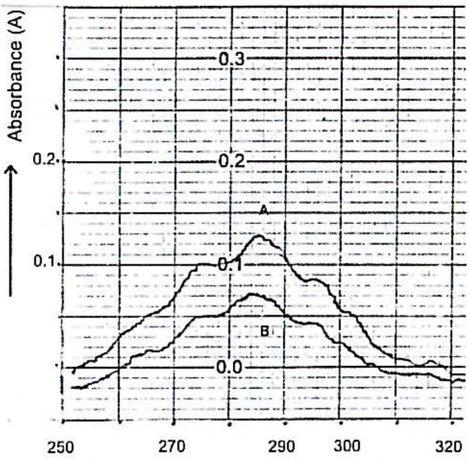

Fig. 2. Absorption of Poly(ACN-CO-AN), 36% ACN in copolymer, Concentration of curve A) (6×10^{-3}g/l), concentration of curve B (4×10^{-3} g/l).

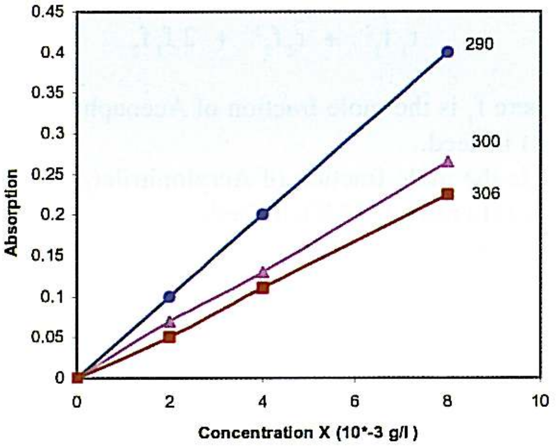

Fig. 3. Absorption (A) vs concentration of poly (Acenaphthalene).

values in Table 1 column (b) are the percentage of ACN of the same copolymer obtained by Nitrogen elemental analysis.

Similarly, values in Table 2 column (a) and (b) are the percentage of Acenaphthalene in the copolymer Poly(ACN-CO-MAN). F is the percentage of Acenaphthalene in the copolymer, (usually F is the mole fraction, here it is expressed as a percent).

Table 1. Composition of Poly(ACN-CO-AN)

Run numbers	ACN : AN feed ratio	% ACN (F) in incopolymer (a)	%ACN (F) copolymer (b)
1	1 : 9	38	36
2	2 : 8	47	48
3	3 : 6	66	76
4	4 : 6	78	84
5	5 : 5	76	82
6	6 : 4	80	89
7	8 : 2	90	91
8	9 : 1	95	94

Table 2. Composition of poly (ACN-CO-MAN)

Run numbers	ACN : MAN	%ACN (a)	% ACN (b)
1	0.05 : 0.09	14	16
2	0.03 : 0.97	07	09
3	0.01 : 0.99	04	05

Monomer reactivity ratios of Poly (ACN-CO-AN) and poly(ACN-CO-MAN) can be calculated by using the copolymer composition equation[8], which gives the copolymer composition as the mole fraction of monomer in the copolymer.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + r_2 f_2^2 + 2 f_1 f_2} \qquad (2)$$

where f_1 is the mole fraction of Acenaphthalene (ACN) in feed.

f_2 is the mole fraction of Acrylonitrile(AN), or Methacrylonitrile (MAN), in feed.

r_1 is the monomer reactivity ratio of Acenaphthalene (ACN).

r_2 is the monomer reactivity ratio of Acrylonitrile (AN) or Methacrylonitrile (MAN).

F_1 is the mole fraction of Acenaphthalene (ACN) in the copolymer.

The plots of r_1 *vs* r_2 for run numbers 1,2,7 and 8 are shown in figure 4, for poly(ACN-CO-AN). Four lines crossed at (P) ($r_1 = 2.40$) and ($r_2 = 0.10$). By using these values the percentages of ACN in copolymers were calculated by equation (2)[7] and found to be in good agreement with UV data method.

The values of ACN composition in poly(ACN-CO-AN) which are listed in Table 1 were calculated by the Nitrogen weight % analysis as shown in Table 3 and figure 5.

Table 3. Weight percent Nitrogen and mole fractions of polymers.

Run No.	ACN :AN Feed ratio	Analytical (wt%) (a)	F_1 ACN (b)	F_1 AN (c)
1	1 : 9	10.09	0.36	0.64
2	2 : 8	7.22	0.48	0.52
3	3 : 6	2.48	0.76	0.24
4	4 : 6	1.58	0.84	0.16
5	5 : 5	1.83	0.82	0.18
6	6 : 4	1.02	0.89	0.11
7	8 :2	0.89	0.91	0.09
8	9: 1	0.68	0.94	0.06

(a) Theoretical wt. % N2 in the copolymer (ACN –CO – AN).
(b) Mole fraction ACN in the copolymer obtained by (1- F_{AN}).
(c) Mole fraction AN in the copolymer,obtained by reading the value of weight (N_2 %) directly from the graph (Fig. 5).

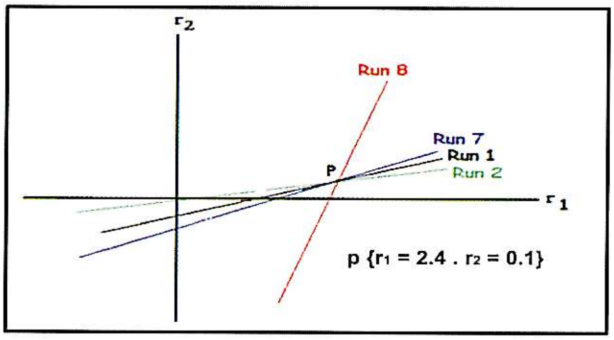

Fig. 4. Monomer reactivity ratios, r_1 *vs* r_2 in Poly (ACN-CO-AN).

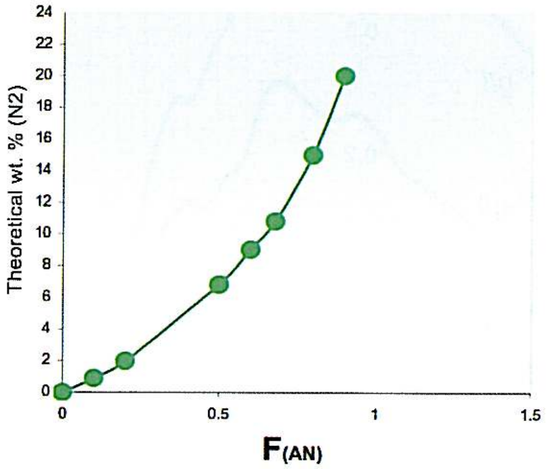

Fig. 5. Theoretical weight % (N2) *vs* Nitrogen F_{AN}.

The plots of mole fractions of ACN [F_1] in poly(ACN-CO-AN) and poly (ACN-CO-MAN) vs. the mole fraction of ACN in feed (f_1) are shown in figure 6 and figure 7.

Curve (A) shows the value calculated from the copolymer composition equation, where r_1 is 2.40 and r_2 is 0.1 for copolymer poly(ACN-CO-AN), r_1 = 2.38 and r_2 = 0.15 for the copolymer poly(ACN-CO-MAN).

Curve (B) shows the experimental data from UV spectra. The close agreement between curve (A) and curve (B) indicates the utility of quantitative UV analysis for the copolymers used in this work.

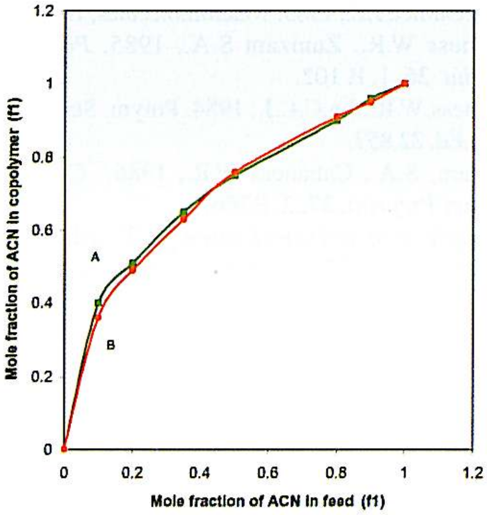

Fig. 6. mole fraction of ACN (F1) in poly (ACN-CO-AN) vs. mole fraction of ACN in feed f1. Curve A calculated from copolymer composition equation, Curve B calculated from UV absorption data.

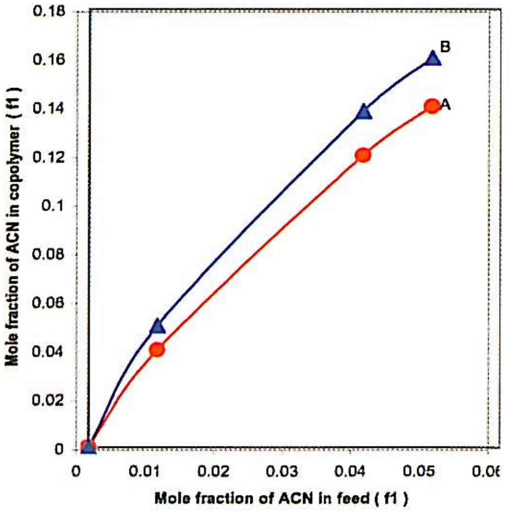

Fig. 7. mole fraction of ACN (F1) in poly (ACN –CO-MAN) *vs* mole fraction of ACN in feed f1,Curve A calculated from copolymer composition equation, curve B calculated from UV absoprtion data.

It is well known in radical copolymerization that when the $\Sigma r_1 . r_2$ product is zero or less than one, a perfect alternating copolymer is obtained, but when $\Sigma r_1 . r_2$ product is equal to one an ideal random copolymer is obtained. Since the product of the reactivity ratios $\Sigma r_1 . r_2$ for the ACN-AN copolymer is less than one and close to zero (2.4 x 0.1 = 0.2) then the copolymer has the tendency to alternate.

It is possible to determine the degree of alteration as well as the distribution of various monomer sequences in the copolymer chain in quantitative manner. Once the r_1, r_2, f_1, f_2, and F (% ACN) in the copolymer are known, it is possible to determine the sequence distribution. The calculation is based on the run number (R) which is defined as " The average number of uninterrupted monomer sequence (or runs) that occur in a copolymer chain per 100 monomer units" derived by Harwood and Ritchey as follows[8].

$$R = \frac{200}{2 + r_1 . f_1/f_2 + r_2 . f_1/f_2} \qquad (3)$$

where f_1 and f_2 are the mole fraction of ACN and AN in feed respectively and $r_1.r_2$ are the monomer reactivity ratios of ACN and AN respectively.

The sequence distribution (Triads) can be calculated by the following relationship [8] :

$$F_{111} = \frac{[\,f1 - R/200\,]^2}{(\,f_1)^2} \qquad (4)$$

$$F_{212} = \frac{[R/200]^2}{(\,f_1\,)^2} \qquad (5)$$

$$F_{121} = \frac{[R/200]^2}{(\,f_2\,)^2} \qquad (6)$$

$$F_{222} = \frac{[\,f_2 - R/200]^2}{(\,f_2\,)^2} \qquad (7)$$

$$F_{112} + F_{211} = \frac{R/100\ [f_1 - R/200]}{(\,f_1\,)^2} \qquad (8)$$

$$F_{122} + F_{221} = \frac{R/100\ [f2 - R/200\,]}{(\,f_2\,)^2} \qquad (9)$$

$$\Sigma F_{ijk} = 2.0$$

The results of this calculation for triads are listed in table 4.

The average lengths of a given sequence can be calculated by: ACN= r x f1/f2 + 1

The sequence lengths of ACN &AN units in a

Table 4. Calculation for the triad fractions of poly (ACN-CO-AN)

(R)	Feed	ratio	F111	F212	F121	F222	F112+ F211	Total
67	2 : 8	0.25	0.97	0.20	0.28	0.0	0.22	1.92
58	3 : 6	0.02	0.70	0.18	0.32	0.20	0.49	1.91
53	4 : 6	0.12	0.44	0.19	0.32	0.31	0.41	1.80
44	5 : 5	0.31	0.19	0.19	0.31	0.49	0.49	1.98
35	6 : 4	0.50	0.08	0.18	0.33	0.38	0.49	1.97
17	8 : 2	0.79	0.01	0.18	0.32	0.18	0.47	1.95
08	9 : 1	0.90	0.17	0.16	0.36	0.08	0.48	1.98

copolymer of 47% ACN (feed ratio 2:8) are shown to be 1.6 and 1.4 respectively. These are in close agreement with the sequence calculated in table 4 indicating the highly alternating character of the (ACN-CO-AN) copolymer. These results of the sequence lengths and copolymer composition equation together with the quantitative absorption data give a good conclusion to support our evidence that alternating copolymers allow stacking chromophores outside the main coil of the copolymer and increase the efficiency of the energy (Exciton) to migrate along the chromophores of the copolymer so that energy may be transmitted or trapped.

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