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7. Appendix

7.1. UV measurment of the determination of the equillibrium constant of the electron donor-acceptor complexation between styrene and acceptor monomers.



Fig.7.1.1 The overall observed UV absorbance of MA+ST in CCl₄ solution samples with various donor concentration [ST] and constant [MA]=2.5617x10⁻³M at room temperature.



Fig.7.1.2 The UV absorbance of MA-ST complex and acceptor (MA) of MA+ST/CCl₄ solution samples with constant [MA]=2.5617x10⁻³M and varied [ST]=0.79-4.45M.

No.	g(ST)	[D] ₀	1/[D] ₀	A^{λ}_{ca}	ca		[A] ₀ /(A	$[A]_0/(A^{\lambda}_{ca} - A^{\lambda}_{OA})$		
				λ =312	314	315nm	λ =312	314	315nm	
0	0.0			$A^{\lambda}_{O} = 0.1113$	0.1044	0.1031				
OA	0.0			$A^{\lambda}_{OA} = 0.1741$	0.1676	0.1627				
OD	0.8174	1.5696	0.6371	A_{OD}^{λ} =0.2268	0.1698	0.1516				
3	0.4138	0.7946	1.2585	0.5021	0.4681	0.4541	0.0078	0.0085	0.0088	
4	0.523	1.0043	0.9957	0.5532	0.5142	0.5026	0.0068	0.0074	0.0075	
5	0.646	1.2405	0.8061	0.6078	0.5694	0.5526	0.0059	0.0064	0.0066	
6	1.0558	2.0274	0.4932	0.8258	0.7809	0.7549	0.0039	0.0042	0.0043	
7	1.5693	3.0135	0.3318	1.0226	0.9616	0.9299	0.003	0.0032	0.0033	
8	2.0173	8.8669	0.2586	1.1634	1.0991	1.0626	0.0026	0.0028	0.0028	
9	2.3188	4.4528	0.2246	1.2847	1.2369	1.2055	0.0023	0.0024	0.0025	

Tab.7.1.1 Determination of the equilibrium constant (K) of the MA-ST complexation in CCl₄

 $O = Solvent = CCl_4$

OA= Acceptor-Solvent solution = MA-CCl4 $[A]_0 = [MA]_0$ OD= Donor-Solvent solution = ST-CCl4 $A^{\lambda}_{ca} = Abs$ 3-9 = $[MA]_{const.} + [ST]_{varied} / CCl_4$ samples (5ml) $= A^{\lambda}_{sample}$ g(ST) = mass of styrene in 5 ml solution sample $A^{\lambda}_{sample} = A^{\lambda}_{sample}$

$$\begin{split} & [A]_0 = [MA] = 2.5617 \times 10^{-3} \text{ mol/l} \\ & A^{\lambda}_{ca} = \text{Absorbance of complex and acceptor} \\ & = A^{\lambda}_{sample} - \{g(ST).[A^{\lambda}_{OD} / g(ST)_{OD}]\} \\ & A^{\lambda}_{sample} = \text{overal observed absorbance of} \\ & \text{ solution sample} \end{split}$$

Wavelength (λ) in nm	Slope (a)	Intercept (b)	Regression (R)	<i>K</i> = b/ a
312	0.005 4437	0.001 22	0.996 68	0.224
314	0.006 0485	0.001 2024	0.996 79	0.199
315	0.006 201	0.001 2539	0.997 06	0.202

The equilibrium constant of MA-ST complexation in CCl_4 at room temperature :

(determined by UV spectroscopy using Ketchar equation) K = 0.208

 $K = 0.208 \pm 0.015$ l/ mol



Fig.7.1.3 The overall observed UV absorbance of MA+ST in DMF solution samples with various donor concentration [ST]=0.99-6.90M and [MA]=4.8869x10⁻³M at room temperature.



Fig.7.1.4 The UV absorbance of MA-ST complex in MA+ST/DMF solution samples with constant [MA]=4.8869x10⁻³M and varied [ST]=1.95-6.90M.

Tab.7.1.2 UV absorbance of MA(A or 0)-ST(D or 1) complex in DMF by varied MA mole fraction of $f_0 = 0.0 - 1.0$ in MA+ST/ DMF. [MA+ST] = 2.000 ± 0.001 M. (Data of continuos variation plot in Fig.4.1.2)

No. f_0 [MA] g(MA) g(ST)					Abso	orba	ance of M	A-ST co	omplex =	- Α ^λ c						
		in M			λ =3	370	371	372	373	374	375	376	377	378	379	380nm
00					$A^{\lambda}_{OO} = 0.04$.95	0.0489	0.0485	0.0492	0.047	0.0469	0.0466	0.0476	0.0471	0.0457	0.0458
					$a^{\lambda}OA = 0.043$	3	0.0425	0.0414	0.0416	0.041	0.0401	0.0394	0.0396	0.0389	0.0382	0.0382
					$b_{OA}^{\lambda} = 0.134$	45	0.1204	0.1084	0.0972	0.0869	0.0785	0.0706	0.0623	0.0569	0.0522	0.0472
0 =OD 2 4 5 6 8 10=OA	0.0 0.2 0.4 0.5 0.6 0.8 1.0	0.0 0.4 0.8 1.0 1.2 1.6 2.0	0.0 0.1961 0.3922 0.4903 0.5883 0.7845 0.9806	$\begin{array}{c} 1.0415\\ 0.8332\\ 0.6249\\ 0.5208\\ 0.4166\\ 0.2083\\ 0.0 \end{array}$	0.00 0.63 0.94 0.97 0.94 0.63 0.01	30 37 21 71 20 27 63	$\begin{array}{c} 0.0025\\ 0.5747\\ 0.8621\\ 0.8910\\ 0.8583\\ 0.5768\\ 0.0170\\ \end{array}$	0.0025 0.5246 0.7829 0.8112 0.7802 0.5261 0.0197	$\begin{array}{c} 0.0034\\ 0.4771\\ 0.7131\\ 0.7359\\ 0.7099\\ 0.4736\\ 0.0206\end{array}$	0.0020 0.4330 0.6494 0.6675 0.6447 0.4329 0.0216	$\begin{array}{c} 0.0045\\ 0.3929\\ 0.5872\\ 0.6068\\ 0.5841\\ 0.3909\\ 0.0227\end{array}$	0.0043 0.3552 0.5327 0.5458 0.5281 0.3528 0.0241	$\begin{array}{c} 0.0031 \\ 0.3207 \\ 0.4813 \\ 0.4951 \\ 0.4769 \\ 0.3200 \\ 0.0256 \end{array}$	$\begin{array}{c} 0.0039\\ 0.2887\\ 0.434\\ 0.4460\\ 0.4267\\ 0.2856\\ 0.0246\end{array}$	$\begin{array}{c} 0.0047\\ 0.2615\\ 0.3909\\ 0.4008\\ 0.3859\\ 0.2555\\ 0.0242 \end{array}$	0.0032 0.2346 0.3537 0.3614 0.3456 0.2308 0.0252
$A^{\lambda}{}_{c} = A$ $= A$	Α ^λ samp Α ^λ samp	$he - A^{\lambda}_{oa}$	- Α ^λ _{od} +	A ^λ OO	Α ^λ ο Α ^λ ο	 ю≃ a =	$A^{\lambda}_{od} \simeq$ $A^{\lambda}_{OA} =$	A^{λ}_{OD} f a^{λ}_{OA} +	for $\lambda = 37^{\circ}$ $b^{\lambda}OA \cdot [$	0 - 380 n MA] (2	um A ^λ OA wa	as callibr	ated vs. [MA])		
A^{λ}_{samp}	_{le} =ove	ral observ	ed absort	oance of	solution sampl	e			$A^{\lambda}OO =$	Absorba	ance of D	MF				
A^{λ}_{oa}	= Ab	sorbance	of MA in	MA+ST	7 DMF solution	on s	ample		$A^{\lambda}OA =$	= Absorba	ance of N	1A in DN	٨F			
A^{λ}_{od}	= Ab	sorbance	of ST in l	MA+ST/	DMF solution	n sa	mple		$A^{\lambda}OD =$	- Absorb	ance of S	T in DM	F			



Fig.7.1.5 The equilibrium constant (K) of MA-ST complexation in different solvents vs. the dielectric constant (ε) of the corresponding solvent. (* estimated value).

Tab.7.1.3. Empirical correlation between the MA-ST complexation equilibrium constant (K) and the dielectric constant (ϵ) of the solvent for the estimation of K in DMF.

Solvent Dielectric constant (ε) ⁸³		<i>K</i> [l/mcl]	(T/method)	<i>K</i> ^{-2.5}	
<i>n</i> -Hexan	1.9	0.336	30°C / NMR ¹¹	15.281	
Cyclohexan	2.0	0.25	60°C / NMR ¹³	32.000	
Carbon tetrachloride	2.2	0.21	23ºC / UV [this work]	49.483	
Chloroform	4.8	0.093	23°C / UV ⁴³	379.13	
Methyl Ethyl Ketone	18.5	0.045	23°C / UV ²⁴	2327.9	
DMF	36.7	0.035	23°C / estimated	4363.4	
$K^{-2.5} = -239.9$	95 + 135.17 x	ε (Re	gression =0.999 83)		



Fig.7.1.6 The overall observed UV absorbance of CA+ST in CCl₄ solution samples with various donor concentration [ST]=0.40-4.96M and constant [CA]=2.7834x10⁻³M at room temperature.



Fig.7.1.7 The UV absorbance of CA-ST complex and acceptor (CA) of CA+ST/CCl4 solution samples with constant [CA]=2.7834x10⁻³M and varied [ST]=0.40-4.96M.

No.	g(ST)	[D] ₀	1/[D] ₀		A^{λ}_{ca} $\lambda = 311$	312	313	314	315	316	317 nm
0	0.0			$A^{\lambda}O =$	0.0267	0.0262	0.0277	0.0284	0.0262	0.0288	0.0278
OA	0.0			$A^{\lambda}OA =$	=0.0911	0.0899	0.0877	0.0886	0.082	0.0835	0.0822
OD	0.5193	0.9972	1.0028	A_{OD}^{λ} =	=0.149	0.1156	0.0954	0.0819	0.0776	0.0699	0.0656
4	0.3262	0.6264	1.5964		0.2584	0.2446	0.2343	0.2238	0.2103	0.1984	0.1901
5	0.3683	0.7072	1.4139		0.2793	0.2675	0.2532	0.2404	0.2292	0.2165	0.2073
6	0.4305	0.8267	1.2097		0.306	0.2913	0.2782	0.2633	0.2469	0.2344	0.2231
7	0.5266	1.0112	0.9889		0.3555	0.3397	0.3242	0.3078	0.2858	0.2748	0.2604
8	0.6627	1.2726	0.7858		0.4041	0.3813	0.3603	0.3442	0.3211	0.3055	0.2842
9	0.8535	1.6390	0.6101		0.4951	0.452	0.4268	0.4046	0.3753	0.3538	0.3336
10	1.302	2.5002	0.4000		0.6178	0.584	0.5499	0.5179	0.4764	0.4517	0.4229
11	2.5807	4.9557	0.2018		0.9293	0.9017	0.8506	0.7945	0.727	0.6833	0.6382
		. <u>.</u>			[A] ₀ / (.	$\Lambda^{\lambda}_{ca} - A^{\lambda}$	°OA)				
No.					λ =311	312	313	314	315	316	317nm
4					0.0166	0.0180	0.0190	0.0206	0.0217	0.0242	0.0258
5					0.0148	0.0157	0.0168	0.0183	0.0189	0.0209	0.0223
6					0.0130	0.0138	0.0146	0.0159	0.0169	0.0185	0.0198
7					0.0105	0.0111	0.0118	0.0127	0.0137	0.0145	0.0156
8					0.0089	0.0096	0.0201	0.0109	0.0116	0.0125	0.0138
9					0.0069	0.0077	0.0082	0.0088	0.0095	0.0103	0.0111
10					0.0053	0.0056	0.0060	0.0065	0.0071	0.0075	0.0082
11					0.0033	0.0034	0.0036	0.0039	0.0043	0.0046	0.0050

Tab.7.1.4 Determination of the equilibrium constant of the CA-ST complexation in CCl₄

 $O = Solvent = CCl_4$

OA= Acceptor-Solvent solution = $CA-CCl_4$

OD= Donor-Solvent solution = ST-CCl₄

4-11= [CA]_{const.}+[ST]_{varied} /CCl₄ samples (5ml) g(ST)= mass of styrene in 5 ml solution sample $[A]_0 = [CA] = 2.7834 \times 10^{-3} \text{ mol/l}$ $A^{\lambda}_{ca} = \text{Absorbance of complex and acceptor}$ $= A^{\lambda}_{sample} - \{g(ST).[A^{\lambda}_{OD}/g(ST)_{OD}]\}$ $A^{\lambda}_{sample} = \text{overal observed absorbance of}$ solution sample

<u>Wavelength (λ) in nm</u>	Intercept (b)	Slope (a)	Regression (R)	<u>K= b/ a</u>
311	0.001 3203	0.009 5372	0.999 46	0.138
312	0.001 4049	0.010 226	0.999 2	0.137
313	0.001 5378	0.010 82	0.999 21	0.142
314	0.001 5584	0.011 825	0.999 19	0.132
315	0.001 978	0.012 188	0.999 21	0.162
316	0.001 8153	0.013 69	0.998 24	0.133
317	0.002 1325	0.014 486	0.998 21	0.147

The equilibrium constant of CA-ST complexation in CCl_4 at room temperature :

(determined by UV spectroscopy using Ketelaar equation)

 $K = 0.142 \pm 0.015$ l/ mol



Fig.7.1.8 The overall observed UV absorbance of CA+ST in DMF solution samples with various donor concentration [ST]=0.51-4.22M and [CA]=2.6800x10⁻³M at room temperature.



Fig.7.1.9 The UV absorbance of CA-ST complex in MA+ST/DMF solution samples with constant [CA]=2.6800x10⁻³M and varied [ST]=0.51·4.22M.

No.	g(ST)	[D] ₀	1/[D] ₀	$A^{\lambda}{}_{c}$				[A] ₀ / (A	λ_{c}		
				λ =317	318	319	320nm	λ =317	318	319	320nm
0	0.0		$A^{\lambda}O =$	0.1029	0.1012	0.0972	0.0963				
OA	0.0		$A^{\lambda}OA =$	0.2421	0.232	0.2232	0.2148				
OD			$a^{\lambda}OD =$	0.0498	0.0508	0.0473	0.0492				
			b ^λ OD=	0.0537	0.0491	0.0469	0.0428				
6	0.5183	0.9953	1.0047	0.0725	0.0679	0.0662	0.0602	0.0370	0.0395	0.0405	0.0445
7	0.6593	1.2660	0.7899	0.0945	0.0855	0.0822	0.0767	0.0284	0.0314	0.0326	0.0350
8	0.8812	1.6922	0.5910	0.1187	0.1123	0.1058	0.0998	0.0226	0.0239	0.0253	0.0269
9	1.2926	2.4822	0.4029	0.1668	0.1559	0.1462	0.1353	0.0161	0.0172	0.0183	0.0198
10	2.1953	4.2156	0.2372	0.3206	0.2981	0.2836	0.2668	0.0084	0.0090	0.0095	0.0100
$\overline{O} = OA=$	Solvent = Acceptor-	DMF Solvent s	solution :	= CA-DN	ΛF		[A] ₀ =	[CA]= 2.	6800x10	- ³ mol/l	
OD=	Donor-So	lvent sol	ution = S	T-DMF			$A^{\lambda}_{c} = A$	bsorband	ce of com	plex	
6-10	$= [CA]_{con}$	_{st.} + [ST]	varied / I	OMF san	nples (5n	nl)	= A	$\lambda_{sample}^{\lambda}$	- $A^{\lambda}{}_D$ -	$A^{\lambda}OA^{+}$	A ^λ O
g(ST) = mass of	f styrene	in 5 ml s	olution s	ample		A^{λ}_{samp}	_{le} = over solu	al observ tion sam	ed absor	bance of

Tab.7.1.5 Determination of the equilibrium constant of the CA-ST complexation in DMF

 A_{OD}^{λ} vs g(ST)_{OD} was callibrated, so $A_{D}^{\lambda} = a_{OD}^{\lambda} + b_{OD}^{\lambda}$. g(ST)

Wavelength (λ) in nm	Slope (a)	Intercept (b)	Regression (R)	<i>K</i> = b/ a
317	0.036 088	0.000 6257	0.997 42	0.017
318	0.039 013	0.000 570 26	0.998 53	0.015
319	0.039 601	0.001 282 7	0.997 03	0.032
320	0.043 638	0.000 825	0.997 58	0.019

The equilibrium constant of CA-ST complexation in DMF at room temperature : $K = 0.021 \pm 0.015$ l/ mol

(determined by UV spectroscopy using Ketelaar equation)

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7.2. Copolymer preparation.

No fo		a a ml				MA+ST	CCl4		MA+ST / DMF			
No.	f ₀	g (MA)	g (ST)	n (Sc	nl olvent)	t _{reaction} (minute)	g (copolyi	conv. ner) (%)	t _{reaction} (minute)	g (copolyn	conv. ner) (%)	
1	0.00	0.0000	4.16	60	5.37				423	0.4006	9.5	
2	0.01	0.0392	4.12	44	5.42	20.5	0.0467	1.11	106	0.1690	4.01	
3	0.02	0.0784	4.08	827	5.44	16.2	0.0771	1.83	47	0.0981	2.33	
4	0.05	0.1961	3.95	577	5.49	9.1	0.0726	1.75	45	0.2165	5.15	
5	0.10	0.3922	0.37	49	5.56	15.1	0.4303	5.19	38	0.2298	5.48	
6	0.15	0.5884	3.54	11	5.64	8.7	0.0986	2.39	33	0.1263	3.02	
7	0.20	0.7845	3.33	328	5.71	8.4	0.0873	2.12	41	0.2583	6.2	
8	0.25	0.9806	3.12	245	5.79	9.2	0.3115	7.5	42	0.2848	6.85	
9	0.30	1.1767	2.91	162	5.87	8.0	0.1652	4.04	36	0.161	3.88	
10	0.35	1.3728	2.70)79	5.94				30	0.1243	3.01	
11	0.40	1.5689	2.49	96	6.02	11.2	0.2352	5.78	37	0.1079	2.62	
12	0.50	1.9612	2.08	30	6.17	7.7	0.1034	2.56	35	0.1035	2.35	
13	0.60	2.3534	1.66	64	6.33	7.2	0.1204	3.00	38	0.1195	2.94	
14	0.70	2.7456	1.24	98	6.48	7.4	0.1237	3.1	36	0.0618	1.53	
15	0.80	3.1379	0.83	32	6.63	8.2	0.1919	4.83	40	0.0845	2.10	
16	0.90	3.5301	0.41	66	6.79	9.1	0.1084	2.75	41	0.0271	0.68	
Prec Res Rep	cipitati olved i recipit	on solvent n Acetone ation solve	(~ 100 (~ 7 m ent (~ 1) ml) 1) 100 1	ml)	Petrolei boiling Petro	Im spirit (bp.60-80°C) Diethy 0°C) Diethy	l ether (D)	EE) EE)	

Tab.7.2.1. Copolymerisation of ST with MA in CCl₄ and in DMF at 50° C.

[MA+ST]=4.000±0.001 M

 $[AIBN] = 0.0305 \pm 0.0001 \text{ M} = 0.0500_8 \pm 0.0005 \text{ g/} 10 \text{ m}$

Total copolymerisation mixture volume = 10.0 ± 0.1 ml

 f_0 = MA mole fraction in feed

conv. = conversion of copolymerisation

 $t_{reaction}$ = time of reaction, controlled by a stop clock.

					CA+ST/CCl4			CA+ST / DMF			
No.	f ₀	g (CA)	g (ST)	ml (Solvent)	t _{reaction} (minute)	g (copoly:	conv. mer) (%)	t _{reactio} (minut	n g e) (copoly	conv. /mer) (%)	
1	0.00	0.0000	4.1660	5.37				423	0.4006	9.5	
2	0.01	0.0448	4.1244	5.38	176).2106	4.99	239	0.1797	4.26	
3	0.02	0.0897	4.0827	5.39	94).0885	2.1	542	0.2689	6.36	
4	0.05	0.2242	3.9577	5.42	101).1211	2.86	538	0.2594	6.13	
5	0.10	0.4484	0.3749	5.47	160	0.1757	4.14	411	0.0.937	2.2	
6	0.15	0.6725	3.5411	5.53	110	0.1381	3.24	408	0.1495	3.5	
7	0.20	0.8967	3.3328	5.58	85	0.1055	2.46	603	0.124	2.9	
8	0.25	1.1209	3.1245	5.63	106	0.1102	2.56	410	0.148	3.44	
9	0.30	1.3451	2.9162	5.68	125	0.1619	3.75	372	0.0475	1.1	
10	0.35	1.5692	2.7079	5.73	103	0.1362	3.15	407	0.1675	3.87	
11	0.40	1.7934	2.4996	5.78	93	0.1394	3.21	364	0.0622	1.43	
12	0.50	2.2418	2.0830	5.88	120	0.1532	3.5	401	0.113	2.58	
13	0.60	2.6902	1.6664	5.99	96	0.1642	3.73	558	0.0464	1.05	
14	0.70	3.1385	1.2498	6.09	88	0.2207	4.97	584	0.045	1.0	
15	0.80	3.5867	0.8332	6.19	92	0.1686	3.77	2 413	0.0624	1.4	
16	0.90	4.0352	0.4166	6.30	96	0.1557	3.46				
17	0.95	4.2594	0.2083	6.35	354	0.2718	6.02				
Prec Was	cipitatio shing so	n solvent lvent (~ 1	(~ 100 m 00 ml)	l) boili	Petroleu ng Petroleu	ım spirit ım spirit	(bp.60-80°C) (bp.80-110°C)	Dieth Dieth	yl ether (I yl ether (I	DEE) DEE)	

Tab.7.2.2. Copolymerisation of ST with CA in CCl₄ and in DMF at 50° C.

[CA+ST]=4.000<u>+</u>0.001 M

 $[AIBN] = 0.0305 \pm 0.0001 \text{ M} = 0.0500_8 \pm 0.0005 \text{ g/ } 10 \text{ m}$

Total copolymerisation mixture volume = 10.0 ± 0.1 ml

 f_0 = CA mole fraction in feed

conv. = conversion of copolymerisation

 $t_{reaction}$ = time of reaction, controlled by a stop clock.

No.	Solvent Diele	ctric constant $(\varepsilon)^{83}$	t _{reaction} (minute)	g (copolyn	conv. ner) (%)
1	Carbon tetrachloride (CCl ₄)	2.24	5.7	0.1644	4.01
2	Di-n-butyl ether (C ₄ H ₉ -O-C ₄ H ₉	3.06	8.0	0.2731	6.69
3	Chloroform (CHCl ₃)	4.8	5.9	0.304	7.42
4	1,1,1-Trichloroethane (CCl ₃ -Cl	H ₃) 7.52	6.9	0.1588	4.53
5	1,1,2,2-Tetrachloroethane (CHC	Cl ₂ CHCl ₂) 8.2	5.9	0.2805	6.83
6	Methylenechloride (CH_2Cl_2)	8.9	6.5	0.099	2.42
7	1,2-Dichloroethane (CH ₂ Cl-CH	¹ ₂ Cl) 10.36	8.5	0.1748	4.27
8	Methyl ethyl ketone (MEK)	18.51	12.1	0.1675	4.09
9	Acetone (CH ₃ -O-CH ₃)	20.7	16.3	0.2673	6.53
10	N,N-Dimethylformamide (DMF) 36.7	95.9	0.105	2.56

g(MA) = 1.1912

Tab.7.2.3 Copolymerisation of ST with MA in ten diferent solvents at 50°C.

g(AIBN) = 0.05008

[MA]=[ST]=1.000±0.001M, [AIBN]=0.0153±0.0001M, V_{total}=20.0±0.1ml

Precipitation solvent (~ 100 ml)	Petroleum spirit (bp.60-80°C)		
Re-dissolved in Acetone (~ 7 ml)			
Reprecipitation solvent (~ 100 ml)	boiling Petroleum spirit (bp.80)-110°C)	
For the copolymerisation in DMF solut copolymer	tion diethyl ether (DEE) was used fo	or precipita	ating the
2.4. Copolymerisation of ST with	BMA, with DCMA and with	MI at 50	°C.

(copolymer) (%) (min) [BMA]=[ST]=0.5M, [AIBN]=0.0100M=0.0492g 237 0.1666 3.9 g(BMA)=2.6504 $V_{CC14} = 26.88 \text{ml}$ V_{Total} = 30 ml g(ST) = 1.5677Precipitation solvent = Petroleum spirit (bp.60-80°C) and boiling Petroleum spirit (bp.80-110°C) [DCMA]=[ST]=1M, [AIBN]=0.0200M=0.0657g 1 4 5 0 0.1735 3.15 g(DCMA)=3.339 $V_{CHCl3} = 15ml$ g(ST) = 2.083 $V_{Total} = 20 \text{ ml}$ Precipitation solvent = Petroleum spirit (bp.60-80°C) and boiling Petroleum spirit (bp.80-110°C) 4.13 [MI]=[ST]=1M, [AIBN]=0.0200M=0.065⁷g 45.5 0.1691 g(MI) = 1.9416 $V_{CC14} = 16.14$ ml $V_{Total} = 20 ml$ g(ST) = 2.083Precipitation solvent = Petroleum spirit (bp.60-80°C) and Di ethyl ether (DEE)

BMA= bromomaleic anhydride DCMA= dichloromaleic anhydride MI = maleimide

conv.



7.3. ¹³C NMR spectra for the determination of triad distribution and the quantitative determination of linkages configurations.

Fig.7.3.1 DEPT ¹³C NMR subspectra of methine(CH) C3 and methylene(CH₂) C1. [MA+ST]=4M/ CCl4/ 50° C. f_0 =0.01-0.90.



Fig.7.3.2 DEPT ¹³C NMR subspectra of methine(CH) C3 and methylene(CH₂) C1. [MA+ST]=4M/ DMF/ 50°C. f_0 =().00-0.90.



Fig.7.3.3 DEPT ¹³C NMR subspectra of methine(CH) C3 and methylene(CH₂) C1. [MA]=[ST]=1M, polymerized in solvent with dielectric constant ranges ε =2.24- 36.7 at 50°C.

Q laternary C7



Fig.7.3.4 Quaternary ¹³C NMR spectra of C7 and C4 of CA(0) -ST(1) copolymer. [CA+ST]=4M/ CCl₄ / 50° C. f_0 =0.01-0.95.

Quaternary C7



Fig.7.3.5 Quaternary ¹³C NMR spectra of C7 and C4 of CA(0) -ST(1) copolymer. [CA+ST]=4M/ DMF / 50°C. f_0 =0.00-0.80.

7.4. The numerical data of the mole fraction of the triads and the overall copolymer composition.

<u>Scheme 3</u>: Restrictions for setting the initial estimates of the reactivity ratios in the five models due to the non-homopropagation of monomer 0

				Number	of variable
					parameters
1. Terminal Model	<u>ro=0</u>		r ₁		1
2. Penultimate Model	$r_{00} = r_{10} = 0$		r11	r01	2
3. Complex Participati	on <u>K de</u>	termined ir	dependently		
Model	$r_{0} = q_{0} = 0$	s ₀	r1 q1	s ₁	4
4.Complex Dissociatio	n <u>K de</u>	termined ir	dependently		
Model	$r_{0} = q_{0} = 0$	s ₀	r ₁ q ₁	s ₁	4
5.Comppen Model	<u>K de</u>	termined ir	ndependently		7
	$r_{00} = r_{10} = 0$		r ₁₁	r ₀₁	
	<u>qoo= q10= 0</u>	<u>)</u>	q 11	q 01	
	<u>soo= 0</u>	s ₁₀	s ₁₁	s ₀₁	
If there's no penultimate eff	fect, Comppen	model redu	ices to Complex	-participation	n model
	<u>r_00= r_10= r_0</u>	<u>e 0</u>	$r_{11} = r_{01} =$	rı	
	<u>q₀₀= q₁₀= q</u>	<u>to=: 0</u>	$q_{11} = q_{01} =$	= q ₁	
	<u>soo</u> = s ₁₀ = s	0 = 0	$s_{11} = s_{01} =$: s ₁	
If there's no complex additi	on, Comppen	model redu	ces to Penultima	ite model	
	$r_{00} = r_{10} = 0$		r ₁₁	r01	
Reactivity ratios env	volved complex	x equal zero):		
	<u>q_00= q_10</u> = q	$q_{11} = q_{01} = ($)		
	$\underline{s}_{00} = \underline{s}_{10} = \underline{s}$	$11 = s_{01} = 0$			

underlined means fix initial estimate

Tab.7.4.1. The experimental and the for 5 models calculated triad and composition data of MA-ST copolymer prepared in CCl₄. The triad mole fractions were determined from DEPT ¹³C NMR CH₂-subspectra of C1. *K*=0.208(l/mol).

f_0	$F_0 = F_{010}$						$F_{(011+110)}$						
	exp	1	2	3	4	5	exp	1	2	3	4	5	
0.01	0.0988	0.1195	0.1016	0.1007	0.1057	0.1479	0.5117	0.4556	0.5337	0.4338	0.4379	0.5700	
0.02	0.2742	0.2666	0.2486	0.2381	0.2461	0.2661	0.5822	0.4992	0.5508	0.4987	0.4999	0.5411	
0.05	0.5270	0.5381	0.5385	0.5185	0.5245	0.5061	0.4530	0.3880	0.4117	0.4016	0.4005	0.4224	
0.10	0.6810	0.7279	0.7374	0.7308	0.7302	0.7117	0.2980	0.2477	0.2617	0.2492	0.2497	0.2732	
0.15	0.8030	0.8140	0.8238	0.8297	0.8248	0.8149	0.1950	0.1742	0.1843	0.1656	0.1676	0.1840	
0.20	0.8360	0.8630	0.8716	0.8853	0.8780	0.8738	0.1310	0.1302	0.1380	0.1159	0.1187	0.1287	
0.25	0.9855	0.8944	0.9019	0.9200	0.9114	0.9106	0.0145	0.1012	0.1074	0.0838	0.0870	0.0927	
0.30	1.0000	0.9164	0.9227	0.9431	0.9340	0.9349	0.0000	0.0806	0.0856	0.0620	0.0652	0.0682	
0.40	0.9800	0.9450	0.9495	0.9703	0.9617	0.9637	0.0200	0.0534	0.0568	0.0351	0.0381	0.0385	
0.50	1.0000	0.9628	0.9660	0.9843	0.9772	0.9791	0.0000	0.0363	0.0386	0.0203	0.0228	0.0223	
0.60	1.0000	0.9750	0.9772	0.9918	0.9865	0.9880	0.0000	0.0245	0.0261	0.0116	0.0135	0.0129	
0.70	1.0000	0.9838	0.9853	0.9959	0.9923	0.9933	0.0000	0.0159	0.0169	0.0064	0.0077	0.0072	
0.80	1.0000	0.9905	0.9914	0.9981	0.9960	0.9966	0.0000	0.0093	0.0099	0.0032	0.0040	0.0037	
0.90	1.0000	0.9958	0.9962	0.9994	0.9984	0.9987	0.0000	0.0042	0.0044	0.0012	0.0016	0.0014	

f_0	<i>F</i> ₁₁₁ exp	1	2	3	4	5	F ₀ exp	1	2	3	4	5
0.01	0.3895	0.3567	0.3893	0.3894	0.3586	0.2317	0.2618	0.2688	0.2670	0.2691	0.2677	0.3288
0.02	0.1437	0.1792	0.1436	0.1433	0.1782	0.1775	0.3611	0.3507	0.3511	0.3503	0.3503	0.3586
0.05	0.0180	0.0491	0.0257	0.0255	0.0462	0.0957	0.4297	0.4291	0.4307	0.4283	0.4298	0.4072
0.10	0.0200	0.0141	0.0060	0.0059	0.0119	0.0447	0.4536	0.4637	0.4650	0.4633	0.4649	0.4449
0.15	0.0020	0.0061	0.0024	0.0024	0.0046	0.0240	0.4738	0.4765	0.4775	0.4766	0.4778	0.4638
0.20	0.0340	0.0032	0.0012	0.0012	0.0021	0.0138	0.4741	0.4832	0.4839	0.4837	0.4845	0.4748
0.25	0.0000	0.0018	0.0007	0.0007	0.0011	0.0081	0.4982	0.4873	0.4879	0.4881	0.4886	0.4819
0.30	0.0000	0.0011	0.0004	0.0004	0.0006	0.0049	0.5000	0.4901	0.4905	0.4910	0.4913	0.4866
0.40	0.0000	0.0005	0.0002	0.0002	0.0002	0.0018	0.4975	0.4936	0.4939	0.4947	0.4946	0.4924
0.50	0.0000	0.0002	0.0001	0.0001	0.0001	0.0007	0.5000	0.4957	0.4959	0.4968	0.4966	0.4956
0.60	0.0000	0.0001	0.0000	0.0001	0.0000	0.0002	0.5000	0.4971	0.4973	0.4980	0.4978	0.4975
0.70	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.5000	0.4981	0.4982	0.4989	0.4986	0.4986
0.80	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.5000	0.4989	0.4990	0.4994	0.4992	0.4993
0.90	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.5000	0.4995	0.4995	0.4998	0.4997	0.4997

2 = Penultimate Unit Effect model

3 = Complex Participation model

4 = Complex Dissociation model

5 =Comppen model

Tab.7.4.2. The experimental and the for 5 models calculated triad and composition data of MA-ST copolymer prepared in DMF. The triad mole fractions were determined from DEPT ¹³C NMR CH₂-subspectra of C1. *K*=0.035(l/mol).

f_0	F_{010}						$F_{(011+110)}$					
	exp	1	2	3	4	5	exp	1	2	3	4	5
$\overline{0.00}$	0.0000				·		0.0000					<u> </u>
0.01	0.0735	0.0820	0.0566	0.0656	0.0787	0.1236	0.4600	0.4121	0.4923	0.4061	0.4069	0.5602
0.02	0.1893	0.2004	0.1633	0.1716	0.1948	0.2263	0.5916	0.4955	0.5573	0.4938	0.4941	0.5409
0.05	0.4160	0.4575	0.4426	0.4315	0.4523	0.4460	0.5290	0.4347	0.4689	0.4379	0.4378	0.4500
0.10	0.6630	0.6647	0.6749	0.6621	0.6635	0.6486	0.3310	0.2975	0.3199	0.2988	0.2987	0.3198
0.15	0.7810	0.7659	0.7817	0.7779	0.7675	0.7574	0.2190	0.2153	0.2324	0.2141	0.2143	0.2333
0.20	0.8440	0.8254	0.8413	0.8449	0.8286	0.8231	0.1570	0.1636	0.1772	0.1607	0.1610	0.1755
0.25	0.8700	0.8645	0.8790	0.8875	0.8686	0.8662	0.1300	0.1284	0.1394	0.1244	0.1248	0.1353
0.30	0.9020	0.8921	0.9049	0.9162	0.8967	0.8963	0.0980	0.1030	0.1121	0.0984	0.0989	0.1062
0.35	0.9680	0.9127	0.9238	0.9365	0.9175	0.9183	0.0320	0.0838	0.0914	0.0789	0.0794	0.0845
0.40	0.9580	0.9285	0.9381	0.9513	0.9334	0.9348	0.0420	0.0689	0.0752	0.0639	0.0644	0.0678
0.50	0.9650	0.9515	0.9585	0.9708	0.9560	0.9579	0.0350	0.0470	0.0514	0.0423	0.0428	0.0442
0.60	1.0000	0.9673	0.9722	0.9825	0.9711	0.9728	0.0000	0.0319	0.0349	0.0278	0.0282	0.0286
0.70	1.0000	0.9788	0.9821	0.9898	0.9817	0.9831	0.0000	0.0207	0.0227	0.0176	0.0179	0.0178
0.80	1.0000	0.9875	0.9895	0.9946	0.9896	0.9905	0.0000	0.0122	0.0134	0.0100	0.0102	0.0101
0.90	1.0000	0.9944	0.9953	0.9978	0.9955	0.9959	0.0000	0.0055	0.0060	0.0043	0.0045	0.0043

f_0	F_{111}						F_0					
	exp	1	2	3	4	5	exp	1	2	3	4	5
0.00	1.0000						0.0000		16 f		·	
0.01	0.4666	0.4374	0.4665	0.4659	0.4381	0.2507	0.2328	0.2353	0.2349	0.2342	0.2346	0.3204
0.02	0.2191	0.2416	0.2198	0.2214	0.2416	0.2033	0.3266	0.3212	0.3212	0.3206	0.3208	0.3476
0.05	0.0540	0.0743	0.0497	0.0474	0.0735	0.1234	0.4049	0.4112	0.4116	0.4117	0.4115	0.3934
0.10	0.0060	0.0227	0.0126	0.0112	0.0219	0.0667	0.4531	0.4536	0.4539	0.4548	0.4543	0.4310
0.15	0.0000	0.0101	0.0052	0.0045	0.0095	0.0408	0.4710	0.4698	0.4700	0.4711	0.4706	0.4512
0.20	0.0000	0.0054	0.0026	0.0023	0.0049	0.0265	0.4798	0.4783	0.4785	0.4797	0.4792	0.4637
0.25	0.0000	0.0031	0.0015	0.0013	0.0028	0.0179	0.4832	0.4835	0.4837	0.4849	0.4844	0.4721
0.30	0.0000	0.0019	0.0009	0.0008	0.0017	0.0123	0.4874	0.4871	0.4872	0.4884	0.4879	0.4782
0.35	0.0000	0.0012	0.0006	0.0005	0.0011	0.0085	0.4960	0.4897	0.4898	0.4910	0.4905	0.4826
0.40	0.0000	0.0008	0.0004	0.0003	0.0007	0.0060	0.4947	0.4916	0.4917	0.4928	0.4924	0.4861
0.50	0.0000	0.0004	0.0002	0.0002	0.0003	0.0029	0.4956	0.4944	0.4944	0.4954	0.4950	0.4909
0.60	0.0000	0.0002	0.0001	0.0001	0.0001	0.0013	0.5000	0.4962	0.4963	0.4971	0.4968	0.4942
0.70	0.0000	0.0001	0.0000	0.0000	0.0000	0.0006	0.5000	0.4976	0.4976	0.4982	0.4980	0.4964
0.80	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.5000	0.4986	0.4986	0.4990	0.4988	0.4980
0.90	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.5000	0.4994	0.4994	0.4996	0.4995	0.4991

- 2 = Penultimate Unit Effect model
- 3 = Complex Participation model
- 4 = Complex Dissociation model
- 5 =Comppen model



Fig.7.4.1 NLLS curve fitting of $F_{(011+110)}$ experimental data to 5 models. (MA+ST/CCl₄)



Fig.7.4.2 NLLS curve fitting of F_{111} experimental data to 5 models. (MA+ST/CCl₄)



Fig.7.4.3 NLLS curve fitting of F_0 experimental data to 5 models. (MA+ST/CCl4)



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Fig.7.4.5 NLLS curve fitting of F_{111} experimental data to 5 models. (MA+ST/DMF)



Fig.7.4.6 NLLS curve fitting of F_0 experimental data to 5 models. (MA+ST/DMF)

Tab.7.4.3. The experimental and the for 5 m odels calculated triad and composition data

of CA-ST copolymer prepared in CCl4 . The triad mole fractions were determined
fromQuaternary ¹³ C NMR spectra of C7. K=0.142(l/mol).

f_0	F_{010}						$F_{(011+1)}$	110)				
	exp	1	2	3	4	5	exp	1	2	3	4	5
0.01	0.1000	0.0261	0.0735	0.0654	0.0659	0.1007	0.2533	0.2400	0.1659	0.3247	0.2921	0.3213
0.02	0.1780	0.0786	0.1381	0.1579	0.1587	0.1755	0.3320	0.3717	0.2763	0.3221	0.4213	0.3197
0.05	0.3380	0.2511	0.2924	0.3565	0.3570	0.3392	0.3305	0.4964	0.4172	0.3143	0.4992	0.3143
0.10	0.4940	0.4617	0.4660	0.5202	0.5198	0.5015	0.3420	0.4604	0.4172	0.3007	0.4319	0.3035
0.15	0.6110	0.5945	0.5809	0.6063	0.6057	0.5986	0.2830	0.3858	0.3587	0.2865	0.3589	0.2906
0.20	0.6540	0.6834	0.6625	0.6625	0.6618	0.6638	0.3050	0.3195	0.3001	0.2718	0.3029	0.2759
0.25	0.6940	0.7467	0.7236	0.7041	0.7035	0.7110	0.2830	0.2654	0.2505	0.2565	0.2605	0.2597
0.30	0.7770	0.7940	0.7709	0.7375	0.7372	0.7471	0.2205	0.2217	0.2096	0.2407	0.2277	0.2425
0.35	0.7840	0.8305	0.8087	0.7660	0.7660	0.7760	0.2115	0.1860	0.1759	0.2243	0.2014	0.2245
0.40	0.7810	0.8596	0.8396	0.7912	0.7914	0.8000	0.2100	0.1564	0.1479	0.2076	0.1800	0.2062
0.50	0.8595	0.9029	0.8870	0.8353	0.8359	0.8388	0.1360	0.1105	0.1044	0.1730	0.1464	0.1694
0.60	0.8590	0.9336	0.9217	0.8740	0.8749	0.8708	0.1340	0.0766	0.0723	0.1374	0.1202	0.1336
0.70	0.8960	0.9566	0.9482	0.9091	0.9101	0.9001	0.1030	0.0507	0.0478	0.1016	0.0975	0.0994
0.80	0.9030	0.9743	0.9691	0.9416	0.9424	0.9296	0.0970	0.0302	0.0285	0.0663	0.0745	0.0664
0.90	0.9880	0.9885	0.9860	0.9718	0.9723	0.9620	0.0250	0.0137	0.0129	0.0322	0.0464	0.0338
0.95	0.9910	0.9945	0.9933	0.9861	0.9864	0.9801	0.0090	0.0065	0.0061	0.0158	0.0271	0.0172

f_0	F_{111}						F_0					
	exp	1	2	3	4	5	exp	1	2	3	4	5
0.01	0.6460	0.7175	0.6780	0.6799	0.6849	0.3109	0.1848	0.1559	0.1832	0.1809	0.1728	0.2916
0.02	0.4900	0.5368	0.5070	0.5071	0.5075	0.2907	0.2560	0.2389	0.2548	0.2550	0.2535	0.3098
0.05	0.3310	0.2654	0.2768	0.2743	0.2688	0.2403	0.3348	0.3512	0.3428	0.3458	0.3528	0.3459
0.10	0.1635	0.1121	0.1446	0.1425	0.1402	0.1798	0.3994	0.4164	0.3984	0.4011	0.4070	0.3827
0.15	0.1060	0.0579	0.0900	0.0892	0.0905	0.1379	0.4294	0.4439	0.4259	0.4273	0.4301	0.4077
0.20	0.0420	0.0334	0.0607	0.0610	0.0644	0.1075	0.4464	0.4590	0.4429	0.4432	0.4436	0.4263
0.25	0.0240	0.0206	0.0428	0.0439	0.0481	0.0847	0.4552	0.4686	0.4546	0.4539	0.4527	0.4407
0.30	0.0030	0.0133	0.0310	0.0327	0.0369	0.0673	0.4701	0.4753	0.4632	0.4617	0.4596	0.4521
0.35	0.0040	0.0089	0.0228	0.0248	0.0286	0.0537	0.4708	0.4801	0.4697	0.4677	0.4651	0.4613
0.40	0.0080	0.0060	0.0168	0.0191	0.0223	0.0430	0.4698	0.4838	0.4749	0.4724	0.4698	0.4687
0.50	0.0080	0.0028	0.0092	0.0116	0.0133	0.0274	0.4812	0.4891	0.4827	0.4794	0.4773	0.4797
0.60	0.0070	0.0013	0.0048	0.0070	0.0075	0.0170	0.4808	0.4927	0.4882	0.4845	0.4833	0.4872
0.70	0.0000	0.0005	0.0022	0.0040	0.0038	0.0101	0.4865	0.4953	0.4922	0.4885	0.4884	0.4923
0.80	0.0000	0.0002	0.0008	0.0020	0.0015	0.0053	0.4876	0.4972	0.4954	0.4920	0.4928	0.4958
0.90	0.0000	0.0000	0.0002	0.0006	0.0003	0.0020	0.5001	0.4988	0.4979	0.4956	0.4966	0.4983
0.95	0.0000	0.0000	0.0000	0.0002	0.0001	0.0008	0.4989	0.4994	0.4990	0.4976	0.4984	0.4993

- 2 = Penultimate Unit Effect model
- 3 = Complex Participation model
- 4 =Complex Dissociation model
- 5 = Comppen model

Tab.7.4.4. The experimental and the for 5 models calculated triad and composition data of CA-ST copolymer prepared in DMF. The triad mole fractions were determined from Quaternary ¹³C NMR spectra of C7. *K*=0.021(l/mol).

f0	F_{010}	1	2	3	4	5	$F_{(011+1)}$	110) 1	2	3	4	5
	P	-	-	5	•	2	enp	•	2	5	•	2
0.01	0.1067	0.0215	0.0656	0.0581	0.0577	0.1037	0.1727	0.2275	0.1772	0.3313	0.3231	0.3184
0.02	0.1659	0.0663	0.1243	0.1448	0.1441	0.1706	0.3713	0.3577	0.2923	0.3286	0.3210	0.3243
0.05	0.3170	0.2229	0.2679	0.3403	0.3398	0.3228	0.4032	0.4927	0.4360	0.3204	0.3146	0.3268
0.10	0.4928	0.4274	0.4359	0.5062	0.5062	0.4804	0.3557	0.4695	0.4354	0.3067	0.3035	0.3170
0.15	0.5965	0.5624	0.5510	0.5923	0.5926	0.5776	0.2941	0.3991	0.3757	0.2929	0.2920	0.3028
0.20	0.6389	0.6552	0.6348	0.6466	0.6470	0.6435	0.2849	0.3336	0.3156	0.2789	0.2799	0.2873
0.25	0.6571	0.7224	0.6986	0.6854	0.6858	0.6912	0.2974	0.2789	0.2643	0.2648	0.2673	0.2711
0.30	0.7281	0.7731	0.7488	0.7156	0.7160	0.7273	0.2488	0.2341	0.2218	0.2504	0.2541	0.2546
0.35	0.7502	0.8127	0.7892	0.7407	0.7410	0.7557	0.2229	0.1970	0.1866	0.2359	0.2404	0.2379
0.40	0.7794	0.8444	0.8226	0.7627	0.7628	0.7786	0.1950	0.1661	0.1572	0.2210	0.2261	0.2209
0.50	0.8221	0.8919	0.8743	0.8014	0.8013	0.8136	0.1694	0.1178	0.1113	0.1904	0.1956	0.1866
0.60	0.8506	0.9259	0.9125	0.8373	0.8369	0.8396	0.1387	0.0820	0.0773	0.1580	0.1625	0.1515
0.70	0.8796	0.9514	0.9420	0.8731	0.8725	0.8606	0.1142	0.0543	0.0512	0.1236	0.1266	0.1155
0.80	0.8592	0.9712	0.9653	0.9110	0.9103	0.8804	0.1289	0.0324	0.0305	0.0864	0.0877	0.0784

f_0	F_{111}			_			F_0					
	exp	1	2	3	4	5	exp	1	2	3	4	5
0.01	0.7206	0.7088	0.6736	0.6829	0.6838	0.3086	0.1618	0.1503	0.1762	0.1681	0.1681	0.2920
0.02	0.4629	0.5255	0.5024	0.5045	0.5043	0.2868	0.2601	0.2324	0.2478	0.2484	0.2484	0.3104
0.05	0.2798	0.2555	0.2742	0.2642	0.2626	0.2346	0.3415	0.3456	0.3370	0.3485	0.3485	0.3459
0.10	0.1116	0.1064	0.1440	0.1351	0.1344	0.1758	0.4014	0.4127	0.3939	0.4035	0.4035	0.3809
0.15	0.1094	0.0546	0.0903	0.0861	0.0865	0.1369	0.4265	0.4412	0.4222	0.4266	0.4266	0.4041
0.20	0.0762	0.0314	0.0615	0.0610	0.0621	0.1093	0.4386	0.4570	0.4398	0.4399	0.4399	0.4212
0.25	0.0455	0.0193	0.0437	0.0460	0.0472	0.0888	0.4462	0.4671	0.4520	0.4488	0.4488	0.4345
0.30	0.0232	0.0124	0.0319	0.0360	0.0372	0.0730	0.4602	0.4740	0.4610	0.4554	0.4554	0.4451
0.35	0.0270	0.0082	0.0236	0.0288	0.0299	0.0604	0.4628	0.4791	0.4679	0.4607	0.4607	0.4538
0.40	0.0257	0.0056	0.0176	0.0234	0.0242	0.0502	0.4672	0.4830	0.4734	0.4651	0.4651	0.4611
0.50	0.0086	0.0026	0.0097	0.0158	0.0159	0.0347	0.4756	0.4885	0.4816	0.4724	0.4724	0.4725
0.60	0.0108	0.0012	0.0051	0.0105	0.0100	0.0236	0.4792	0.4923	0.4874	0.4786	0.4786	0.4810
0.70	0.0000	0.0005	0.0024	0.0066	0.0057	0.0153	0.4837	0.4950	0.4917	0.4843	0.4843	0.4875
0.80	0.0120	0.0002	0.0009	0.0035	0.0026	0.0090	0.4802	0.4971	0.4951	0.4896	0.4896	0.4926

2 = Penultimate Unit Effect model

3 = Complex Participation model

4 = Complex Dissociation model

5 = Comppen model



Fig.7.4.7 NLLS curve fitting of $F_{(011+11)}$ experimental data to 5 models. (CA+ST/CCl₄)



Fig.7.4.8 NLLS curve fitting of F_{111} experimental data to 5 models. (CA+ST/CCl₄)



Fig.7.4.9 NLLS curve fitting of F_0 experimental data to 5 models. (CA+ST/CCl₄)



Fig.7.4.10 NLLS curve fitting of $F_{(011+1+0)}$ experimental data to 5 models.(CA+ST/DMF)



Fig.7.4.11 NLLS curve fitting of F_{111} experimental data to 5 models. (CA+ST/ DMF)



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Fig.4.1.10b Test function a value with its absolutely calculated error range. (MA+ST/DMF)	4.1	42
Fig.4.1.10c Test function b value with its absolutely calculated error range. (MA+ST/DMF) $$	4.1	42
Fig.4.1.10d Test function quantities a and b vesus copolymer composition. (MA+ST/DMF)	4.1	42

Fig.4.1.11 The ST(1) centred triad sequence distribution with respect to the copolymer 4.1 43 composition (F_0). The copolymers of MA with ST were prepared in the nearly non-polar CCl₄ and the highly polar DMF at 50°C. [MA+ST]=4.000M. [AIBN]= 0.0305M. The triad mole fractions were determined from the DEPT ¹³C NMR CH₂ subspectra of C1 carbon. Fig.4.1.12 Mole fraction of the *cis* linkage configurations at the cyclic MA units (F_{cis}) in 4.1 44 MA(0)-ST (1) copolymers prepared in CCl₄ and in DMF vs. MA mole fraction in feed (f_0). Fig.4.1.13 Mole fraction of the *cis* linkage configurations at the cyclic MA units (F_{cis}) in 4.1 46 MA(0)-ST (1) copolymers prepared in CCl4 an 1 in DMF vs. mole fraction of the alternating triad (F_{010}) . Fig.4.1.14 The mole fraction of *cis* linkage configuration at the cyclic MA units (F_{cis}) in 4.1 47 MA-ST copolymers prepared in ten different solvents of the dielectric constants (ε) range from 2.24 to 36.7. F_{cis} was determined by DEPT CH subspectra of C3. [MA] = [ST] = 1.000M.Fig.4.2.1 Determination of the equilibrium constant (K) of CA-ST complexation in 4.2 49 CCl4 at room temperature by UV spectroscopy using the Ketelaar equation. Fig.4.2.2 Determination of the equilibrium constant (K) of CA-ST complexation in 4.2 49 DMF at room temperature by UV spectroscopy using the Ketelaar equation. Fig.4.2.3 Typical ¹³C NMR spectrum of CA(0) -S I(1) copolymer. 4.2 50 $[CA+ST]=4M/CCl_4/50^{\circ}C.f_0=0.95. \text{ conv.}=6.02\%.$ Fig.4.2.4 ¹³C -, Quaternary ¹³C -, DEPT ¹³C - NMR spectra of the alternating 4.2 51 CA(0) -ST(1) copolymer. $[CA+ST]=4M/CCl_4/50^{\circ}C. f_0=0.95. \text{ conv.}=6.02\%$. Fig.4.2.5 Selected Quaternary ¹³C NMR spectra of C7 of CA(0) -ST(1) copolymers 4.2 52 prepared in CCl₄ and in DMF. Fig.4.2.6 Selected Quaternary ¹³C NMR spectra of C4 of CA(0) -ST(1) copolymers 4.2 53 prepared in CCl₄ and in DMF. Fig.4.2.7 NLLS curve fitting of F_{010} experimental data to 5 models. (CA+ST/CCl4) 4.2 56 Fig.4.2.8 NLLS curve fitting of F010 experimental data to 5 models. (CA+ST/DMF) 4.2 56 Fig.4.2.9a Test function quantities a and b vesus composition in feed. (CA+ST/CCl4) 4.2 60 Fig.4.2.9b Test function a value with its absolutely calculated error range. (CA+ST/CCl4) 4.2 60 Fig.4.2.9c Test function b value with its absolutely calculated error range. (CA+ST/CCl4) 4.2 60 Fig.4.2.9d Test function quantities a and b vesus copolymer composition. (CA+ST/CCl4) 4.2 60 Fig.4.2.10a Test function quantities a and b vesus composition in feed. (CA+ST/DMF) 4.2 60 Fig.4.2.10b Test function a value with its absolutely calculated error range. (CA+ST/DMF) 60 4.2

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Fig.4.2.10c Test function b value with its absolutely calculated error range. (CA+ST/DMF)	4.2	60
Fig.4.2.10d Test function quantities a and b vesus copolymer composition. (CA+ST/DMF)	4.2	60
Fig.4.2.11 The ST(1) centred triad sequence distribution with respect to the copolymer composition (F_0). The copolymers of CA with ST were prepared in the nearly non-polar CCl ₄ and the highly polar DMF ε t 50°C. [CA+ST]=4.000M. [AIBN]= 0.0305M. The triad mole fractions were determined from the quaternary ¹³ C NMR spectra of C7 carbon.	4.2	61
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7. Appendix		
Fig.7.1.1 The overall observed UV absorbance of MA+ST in CCl4 solution samples	7.1	81
Fig.7.1.2 The UV absorbance of MA-ST complex and acceptor (MA) of MA+ST/CCl4 solution samples with constant [MA] and varied [ST].	7.1	81
Fig.7.1.3 The overall observed UV absorbance of MA+ST in DMF solution samples with various donor concentration [ST] at room temperature.	7.1	83
Fig.7.1.4 The UV absorbance of MA-ST complex in MA+ST/DMF solution samples with constant [MA] and varied [ST].	7.1	83
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Fig.7.1.6 The overall observed UV absorbance of CA+ST in CCl ₄ solution samples	7.1	86
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Fig.7.1.8 The overall observed UV absorbance of CA+ST in DMF solution samples with	7.1	88

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various donor concentration [ST] at room temperature.		
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constant [CA] and varied [ST].		
Fig.7.3.1 DEPT ¹³ C NMR subspectra of methine(CH) C3 and methylene(CH ₂) C1.	7.3 93	3
[MA+ST]=4M/ CCl4/ 50°C. f ₀ =0.01-0.90		
Fig.7.3.2 DEPT ¹³ C NMR subspectra of methine(CH) C3 and methylene(CH ₂) C1.	7.3 94	4
$[MA+ST]=4M/DMF/50^{\circ}C. f_0=0.00-0.90.$		
Fig.7.3.3 DEPT ¹³ C NMR subspectra of methine(CH) C3 and methylene(CH ₂) C1.	7.3 95	5
[MA]=[ST]=1M, polymerized in solvent wi h dielectric constant ranges $\varepsilon = 2.24$	-	
36.7 at 50 ^o C.		
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[CA+ST]=4M/ CCl4 / 50°C. f0=0.01- 0.95.		
Fig.7.3.5 Quaternary ¹³ C NMR spectra of C7 and C4 of CA(0) -ST(1) copolymer.	7.3 97	7
$[CA+ST]=4M/DMF/50^{\circ}C.f_{0}=0.00-0.80$.		
Fig.7.4.1 NLLS curve fitting of $F_{(011+110)}$ experimental data to 5 models. (MA+ST/	/CCl4)7.4 10)1
Fig.7.4.2 NLLS curve fitting of F_{111} experimenta data to 5 models. (MA+ST/CCl4)	7.4 10)1
Fig.7.4.3 NLLS curve fitting of F_0 experimental data to 5 models. (MA+ST/CCl4)	7.4 10)2
Fig.7.4.4 NLLS curve fitting of $F_{(011+110)}$ experimental data to 5 models.(MA+ST/I	DMF) 7.4 1 0)2
Fig.7.4.5 NLLS curve fitting of F_{111} experimenta' data to 5 models. (MA+ST/DMF)) 7.4 10)3
Fig.7.4.6 NLLS curve fitting of F_0 experimental data to 5 models. (MA+ST/DMF)	7.4 10)3
Fig.7.4.7 NLLS curve fitting of $F_{(011+110)}$ experimental data to 5 models. (CA+ST/	CCl4) 7.4 10)6
Fig.7.4.8 NLLS curve fitting of F_{111} experimenta data to 5 models. (CA+ST/CCl ₄)	7.4 10)6
Fig.7.4.9 NLLS curve fitting of F_0 experimental data to 5 models. (CA+ST/CCl ₄)	7.4 10)7
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Abbreviations

Donor monomer

AB	= allylbenzene
BVE	= n-butyl vinyl ether
CEV	= 2-chloroethyl vinyl ether
MST	$= \alpha$ -methylstyrene

ST = styrene

STI = trans stilbene

Solvent

CCl₄ = carbon tetrachloride

 $CDCl_3 = chloroform-d$

 $CHCl_3 = chloroform$

DEE = diethyl ether

DMF = N,N-dimethylformamide

DMSOd₆= dimethylsulfoxide-d₆

MEK = methyl ethyl ketone

Acceptor monomer

- BMA = bromomaleic anhydride
- CA = citraconic anhydride
- CMA = chloromaleic anhydride
- DCMA= dichloromaleic anhydride
- MA = maleic anhydride

MI = maleimide

Other

AIBN = N,N'-azobisisobutyronitrile

EDA = electron donor-acceptor

DEPT = Distortionless Enhancement by Polarisation Transfer

FID = Free Induction Decay

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NMR = Nuclear Magnetic Resonance

 Γ_1 = longitudinal or spin-latice relaxation time = RD = Recycle Delay