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APPENDIX A

RADIATION DOSIMETRY

Quantitative studies in radiation chemistry require a knowledge of the amount of energy transferred from the radiation field to the absorbing material.

The absorbed dose or total dose is the quantity generally sought and is the amount of energy absorbed per unit mass of irradiated material. The official unit of absorbed dose is the rad, which is defined as an energy absorption of 100 erg g^{-1} or 10^{-2} J Kg^{-1}. The absorbed dose is a direct measure of the energy transferred to the irradiated material and capable of producing chemical or physical change in it; it is determined both by the composition of the material and characteristics of the radiation field.

The absorbed dose rate is the absorbed dose per unit time and has the unit rads, eV g^{-1}, eV cm^{-3}, or grays per unit time, e.g. rads.min^{-1}, grays.min^{-1}, eV.g^{-1}.min^{-1}.

Techniques for measuring ionizing radiation can be divided into absolute and secondary methods. Absolute methods involve direct determination of exposure or absorbed dose from physical measurements of, for example, the energy absorbed (by calorimetry), the ionization produced in a gas, or the charge carried by a beam of charged particles of known energy. The absolute methods are often not suited to routine use and, in practice, secondary dosimeters (e.g. thimble ionization chambers and chemical dosimeters), whose response to radiation is known from comparison with an absolute dosimeter, are generally used.

1. Calorimetry

The most direct way of determining the amount of energy carried by a beam of radiation is to measure the increase in temperature of a block of material placed in the beam, the method originally used by Curie and Laborde to measure the rate of energy release by the radioactive decay of radium. The material must be such that all the absorbed energy is converted to heat, non, for example, being used to initiate chemical reaction. Good thermal conductivity is also necessary and in practice graphite or metals are generally used for this purpose. If the block is of sufficient size to completely absorb the radiation, the rate of temperature increase is related directly to the energy flux density or intensity (erg cm^{-2} sec^{-1}) of the beam. With low intensity radiation, such as that normally available from x-rays and γ-rays sources, the temperature rise is very small and it is important as a check on other, less direct, methods, since the results are obtained directly in energy units.

Radak and Markovic give the range of absorbed dose rate that can be measured in this way as 10^{-7} W g^{-1} (36 rads hr^{-1}) to 10 W g^{-1} (10^{6} rads sec^{-1}). Absorbed dose measurements with calorimeter in which water is the absorbing material have been used to calibrate the Fricky and other aqueous chemical dosimeters described later in this chapter.

2. Chemical Dosimetry

In chemical dosimetry the radiation dose is determined from the chemical change produced in a suitable substrate. Calculation of the dose requires a knowledge of the G value for the reaction or product estimated, which is found by comparing the chemical system with some form of absolute dosimeter. Chemical dosimeters are therefore secondary dosimeters and are used because of their greater convenience. In order to facilitate this conversion and to reduce errors, the dosimeter system is usually chosen so as to have the same atomic composition and density as the sample to be irradiated, as far as this is possible. Aqueous dosimeters, for example, are used if the sample is an aqueous solution, biological material, or organic substance.

For a dosimeter in which radiation induces a chemical change, the mean absorbed dose (D_d) over the volume occupied by the dosimeter is derived as follows. For any system, by definition, G(product) is the number of molecules of product formed per 100 eV energy absorbed and 1 rad corresponds to an energy absorption of 0.01 J Kg^{-1}.

Then;

$$D_d \quad = \quad \text{moles of product formed per kg } \frac{\text{(mol)}}{\text{(kg)}} \times 6.02 \times 10^{23} \text{ (molecules)}$$

$$\frac{\times\ 100}{G\text{ (product)}} \quad \frac{\text{(eV)}}{\text{(molecule)}} \quad \times 1.602 \times 10^{-19} \ \frac{\text{(J)}}{\text{(eV)}} \ \times 100 \ \frac{\text{(kg rad)}}{\text{(J)}}$$

$$= \quad 9.647 \times 10^{8} \times \frac{\text{moles of product formed per kg}}{G\text{ (product)}} \text{ rads} \qquad \textbf{(A-1)}$$

or

$$D_d \quad = \quad 9.647 \times 10^{8} \times \frac{\text{moles of product formed per liter}}{\rho G\text{ (product)}} \text{ rads} \qquad \textbf{(A-2)}$$

Where ρ is the density of the system ($g.cm^{-3}$). Very often the yield of product will be determined spectrophotometrically when, assuming Beer's Law to be obeyed,

$$\text{Moles of product formed per liter} = \frac{\Delta A}{\Delta \varepsilon l} \qquad \textbf{(A-3)}$$

and

$$D_d \quad = \quad 9.647 \times 10^{8} \times \frac{\Delta A}{\varepsilon l \rho G\text{ (product)}} \text{ rads} \qquad \textbf{(A-4)}$$

Where ΔA is the difference in absorbance (or optical density) between the irradiated solution, ε is the difference in molar extinction coefficient (liter mol^{-1} cm^{-1}) of reactant and product at the wavelength being used, and l (cm) is the optical path length (i.e., sample thickness) used when determining the absorbances.

2.1 Fricky (Ferrous Sulfate) Dosimetry

The reaction involved in the Fricky dosimetry is the oxidation of an acid solution of ferrous sulfate to the ferric salts, in the presence of oxygen and under the influence of radiation. The standard dosimeter solution is one containing about 10^{-3} M ferrous sulfate or ferrous ammonium sulfate and 10^{-3} M sodium chloride in air-saturated (2.5×10^{-4} M O_2) 0.4 M sulfuric acid (pH 0.46). The quantities required to prepare such a solution are 0.28 g $FeSO_4.7H_2O$, [or 0.39 g $Fe(NH_4)_2(SO_4)_3.6H_2O$], 0.06 g NaCl, and 22 cm^3 concentrated (95-98%) H_2SO_4 per liter of solution; the solution slowly oxidized and should not be stored longer then a few days.

To determine the absorbed dose (in 0.4 M sulfuric acid) using the Fricky dosimeter, a sample of the dosimeter solution in a container thick enough to ensure electronic equilibrium is placed in the radiation field for a measured length of time, and then the yield of ferric ions measured. To avoid undue wall effects (i.e. so that practically all the secondary electrons contributing to the energy absorption originate of at least 8 mm when γ-radiation is being determined; Burlin using a modified cavity theory, has calculated that with a silica cell and Co^{60}-rays a diameter of 6 cm is needed to reduce the wall effect to below 0.1%. The most common method of measuring the ferric ions formed is by spectrophotometric analysis, comparing the absorbance of the irradiated and nonirradiated dosimeter solutions at the wavelength at which ferric ions show maximum absorption (about 304). The optical readings should be taken soon after the irradiation, so that adventitious oxidation of the solutions is minimized. The mean absorbed dose (D_d) for the volume occuried by the dosimeter solution is given by Eq. A-3 [1].

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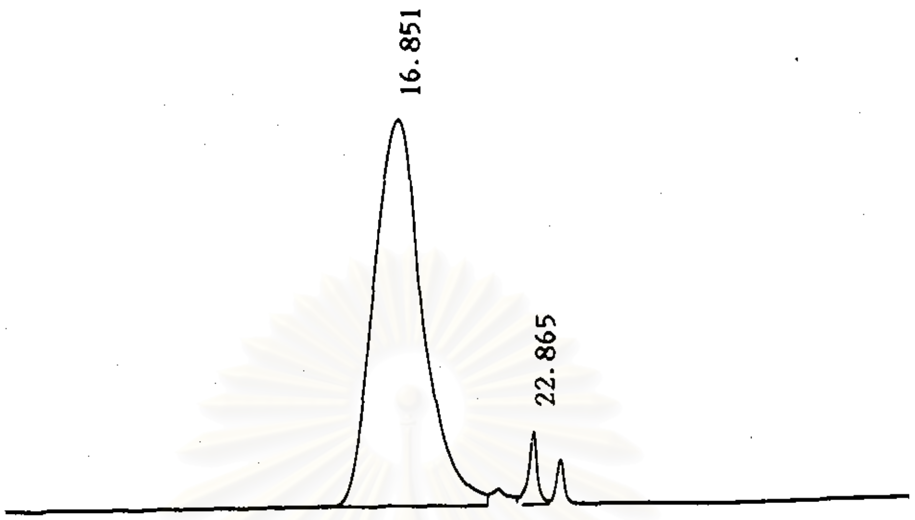
APPENDIX B

GEL PERMEATION CHROMATOGRAPHY OF POLYSTYRENE AND THE POLYSTYRENE COMPOSITES

Average molecular weights and molecular weight distribution of the copolymer were measured by gel permeation chromatography. This technique uses a bed of cross-linked polystyrene-divinylbenzene gel for the separation of the polymer taking place in the voids present in the gel particles. The pore volume available to the larger molecular size species is significantly less than the pore volume available to smaller molecules. This makes the path traveled by the larger molecules shorter than that of small molecules, and the former are thus eluted from the column first. Because the sorting process takes place on the basis of molecular size, a true size distribution of the polymer species takes place.

The GPC chromatograms of PS and composite PS samples are shown in Figures B-1 to B-14.



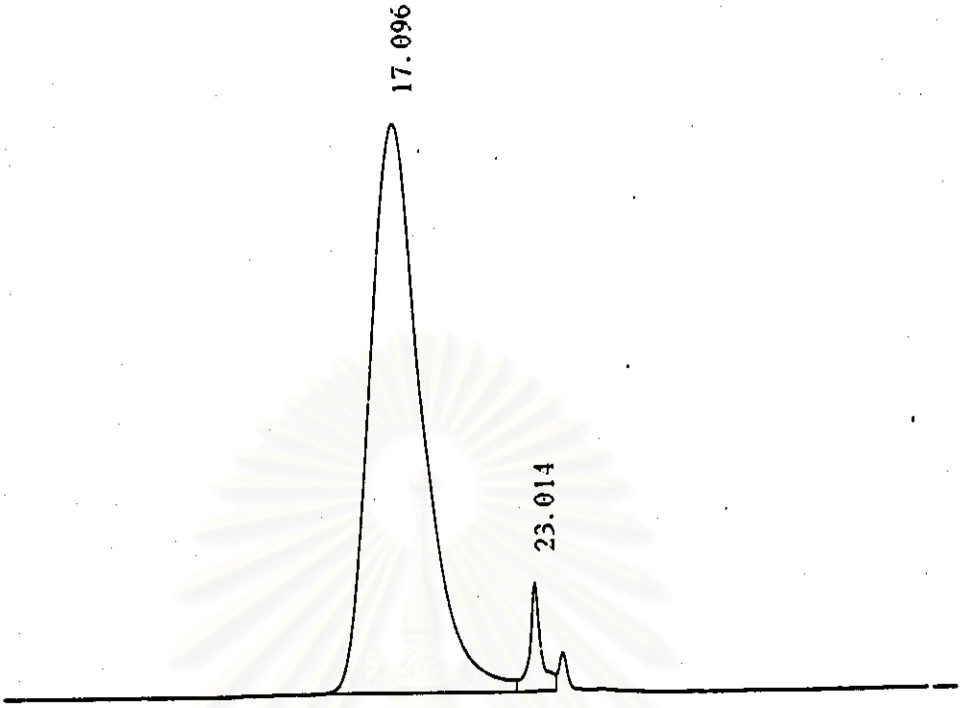
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	16.851	3396078	22968			96.6691
	3	22.865	117017	4172	V		3.3309
			....	....			....
	TOTAL		3513096	27140			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	13.7	12413367	2
top	16.851	358405	22968
end	23.6	181	340

Figure B-1 The GPC chromatograph of control polystyrene sheet.



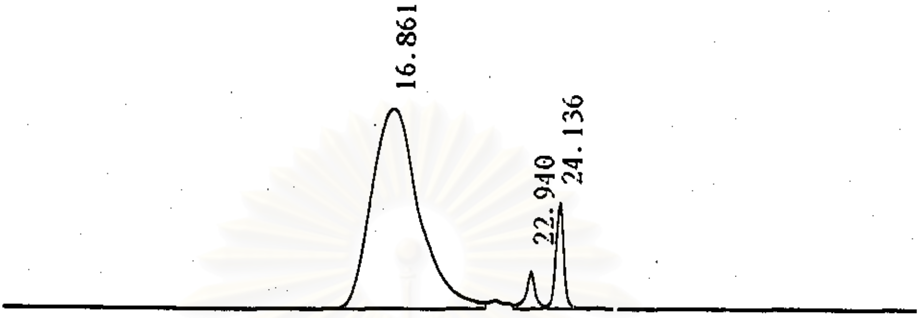
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.096	5342301	34023			95.9848
	2	23.014	223476	6136	V		4.0152
			………	………			………..
	TOTAL		5565777	40159			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	13.6	13891442	2
top	17.096	271963	34023
end	23.9	129	1941

Figure B-2 The GPC chromatograph of polystyrene sheet at 3-month outdoor exposure.



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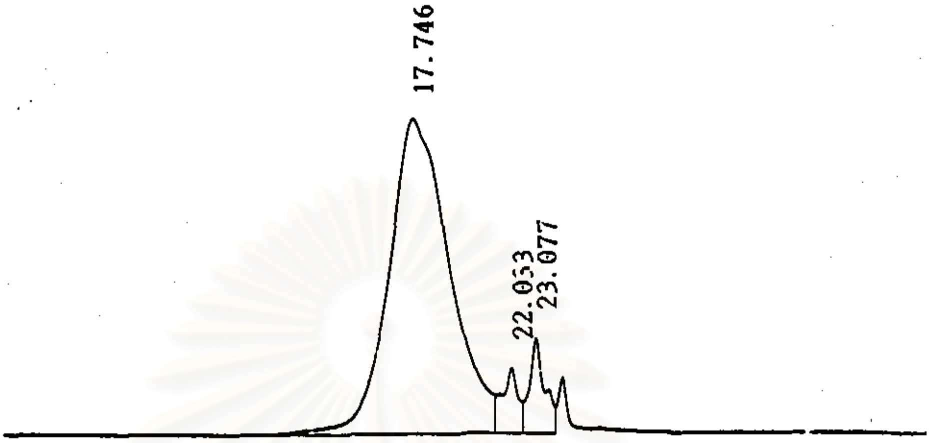
** CALCULATION REPORT**

CH   PKNO      TIME       AREA        HEIGHT   MK   IDNO      CONC
1    1         16.861     3470502     23938                   89.1387
     2         22.940     124003      4312     V              3.185
     3         24.136     298867      12334    V              7.6763
                          .........   .........               ........
          TOTAL           3893371     40584                   100

**TOTAL DATA CHANNEL 1**

PEAK INFORMATION      TIME (min)      MOL. SIZE      HEIGHT
     start            13.95           9370127        2
     top              16.861          354529         23938
     end              25.3            27             89
```

Figure B-3 The GPC chromatograph of polystyrene sheet at 6-month outdoor exposure.



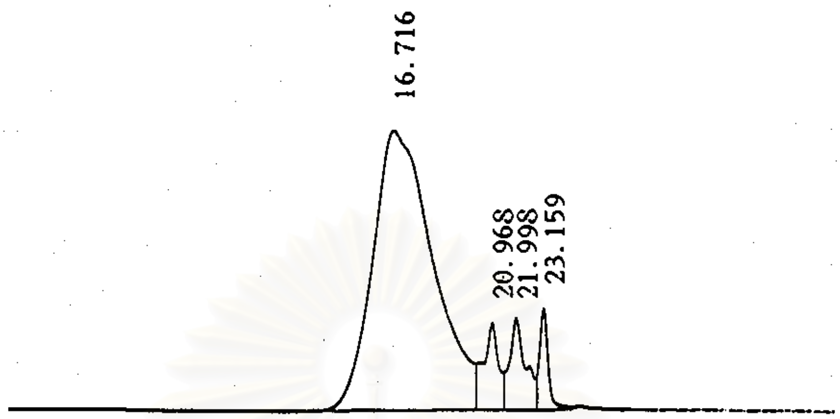
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.746	3470042	18741			88.5682
	2	22.033	188734	3784	V		4.8172
	3	23.077	259158	5488	V		6.6147
			………	………			……..
	TOTAL		3917934	28012			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	11.1	231311616	2
top	17.746	130898	18741
end	23.95	122	3175

Figure B-4 The GPC chromatograph of polystyrene sheet at 100 kGy absorbed dose.



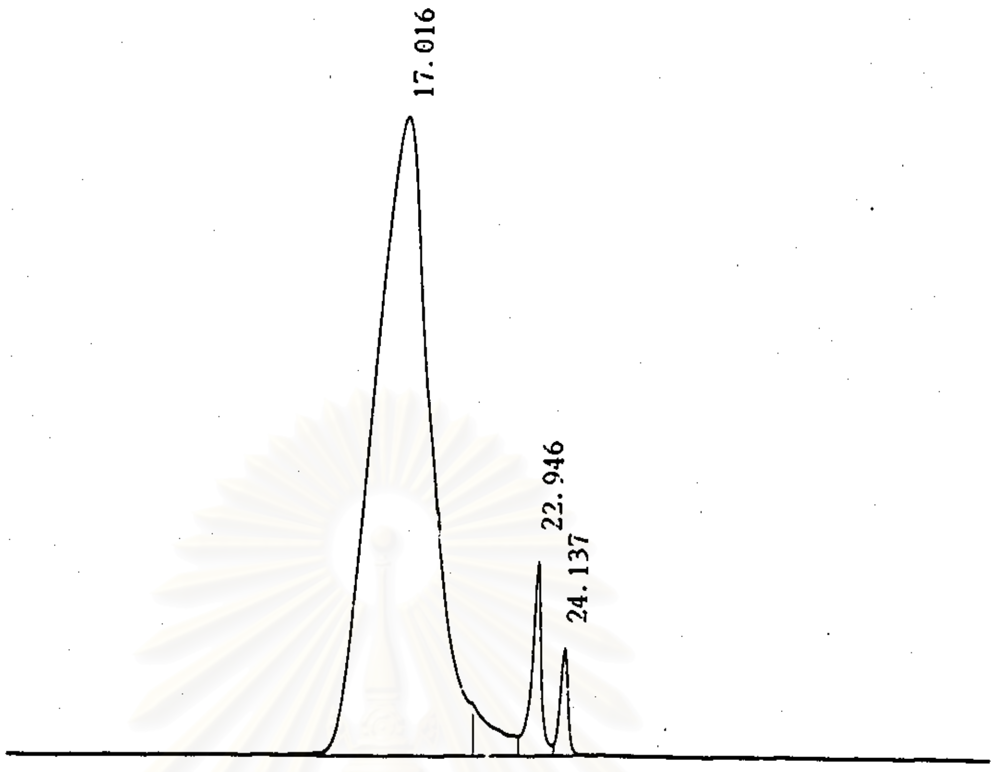
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	16.716	3072931	16742			82.442
	2	20.968	236748	5061	V		6.3516
	3	21.998	263428	5243	V		7.0674
	4	23.159	154278	5918	V		4.139
			....	....			....
	TOTAL		3727384	32963			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	12.95	28861900	1
top	16.716	417033	16742
end	24.4	73	315

Figure B-5 The GPC chromatograph of polystyrene sheet at 300 kGy absorbed dose.



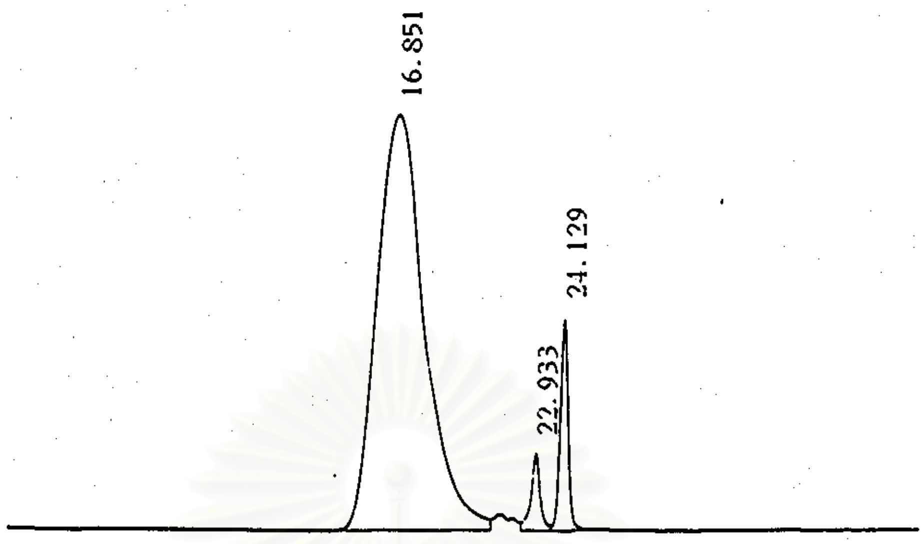
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.016	9814432	66545			95.2599
	2	22.946	10905	10905	V		3.2226
	3	24.137	156347	6118	V		1.5175
			....	....			....
	TOTAL		10302795	83568			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	13.7	12413367	1
top	17.016	297687	66545
end	25.35	25	69

Figure B-6 The GPC chromatograph of polystyrene sheet at 10-hour UV irradiation time.



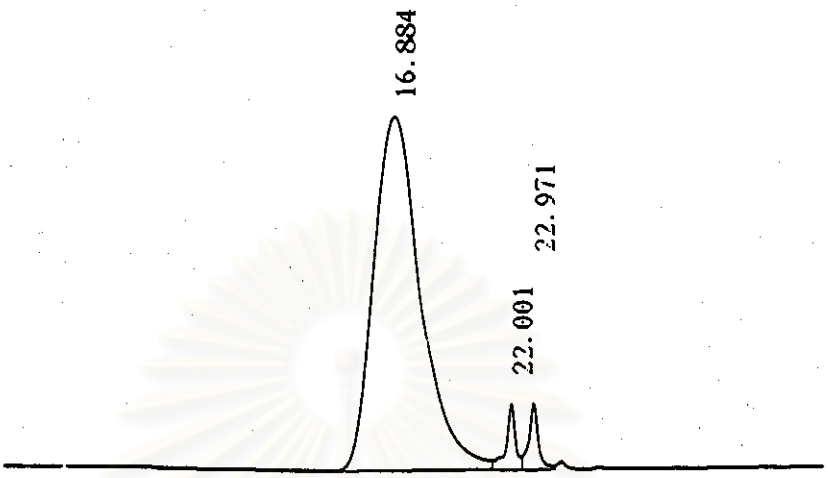
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	16.851	3611187	24879			89.5448
	3	22.933	125297	4440	V		3.1069
	4	24.129	296343	12159	V		7.3483
			....	....			....
	TOTAL		4032828	41478			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	14	8857593	1
top	16.851	358405	24879
end	25.4	24	77

Figure B-7 The GPC chromatograph of polystyrene sheet at 21-hour UV irradiation time.



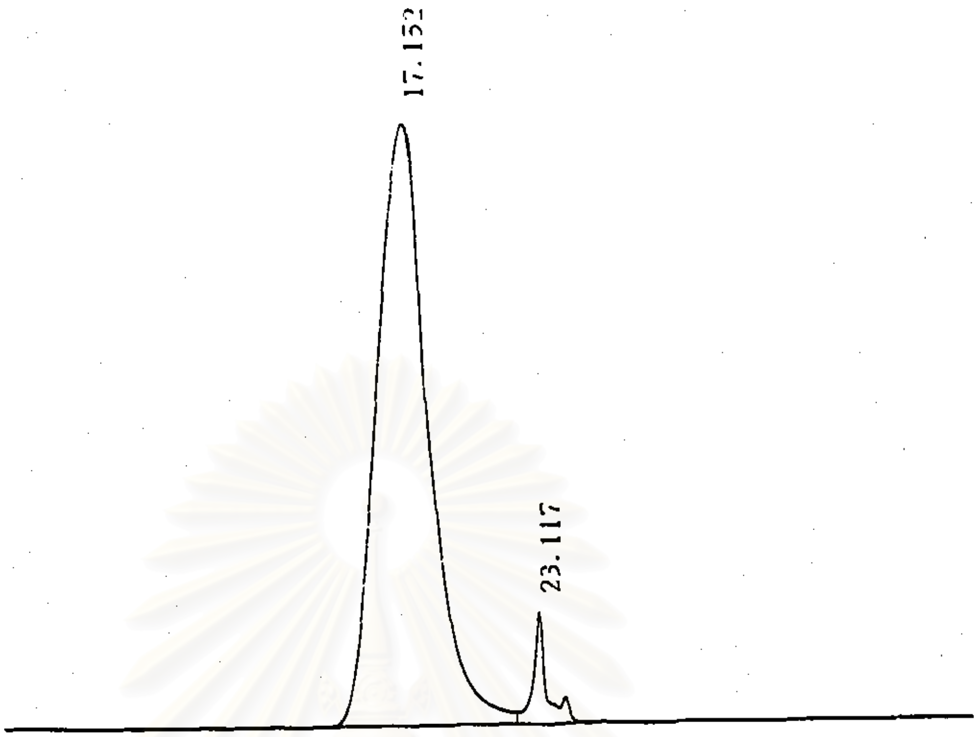
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	16.884	3016496	21079			93.0365
	2	22.001	113775	3561	V		3.5091
	3	22.971	112001	3779	V		3.4544
			....	....			....
	TOTAL		3242272	28419			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	14.15	7482191	2
top	16.884	345214	21079
end	23.9	129	392

Figure B-8 The GPC chromatograph of control PS-G15/36 sheet.



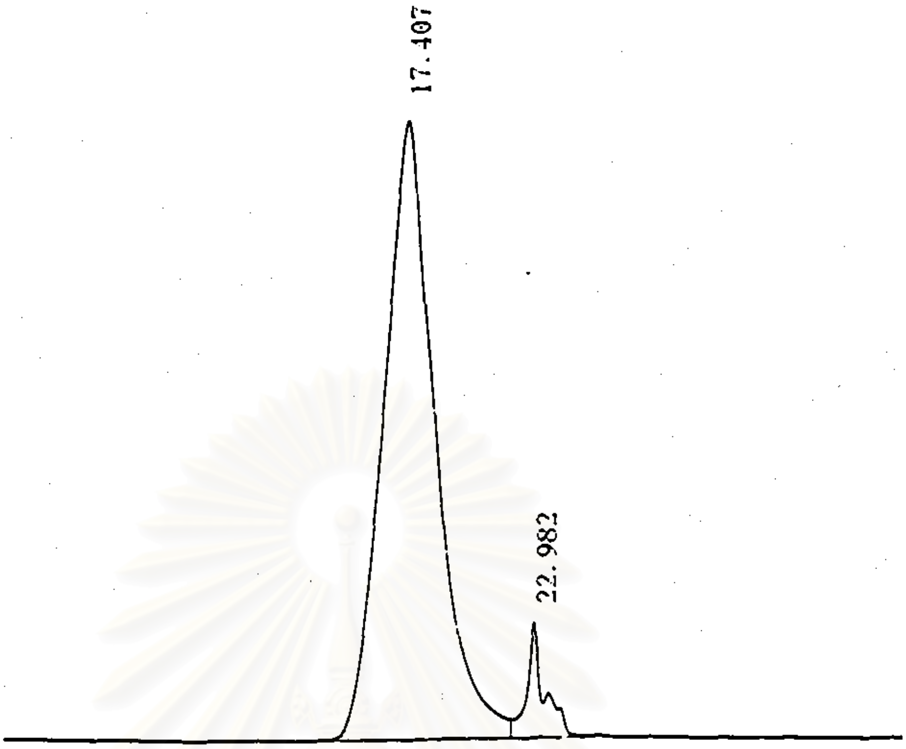
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.152	5576085	35744			95.1945
	2	23.117	281487	6503	V		4.8055
			…………	……..			……….
	TOTAL		5857572	42247			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	13.7	12413367	3
top	17.152	255549	35744
end	25.45	23	65

Figure B-9 The GPC chromatograph of PS-G15/36 sheet at 3-month outdoor exposure.



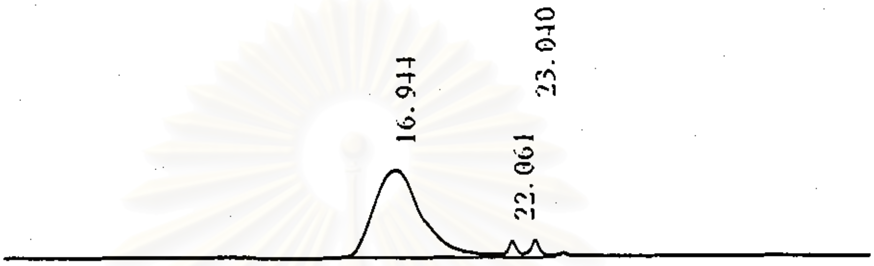
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.407	5838173	36921			94.2099
	2	22.982	358810	6740	V		5.7901
			…………	………			………
	TOTAL		6196983	43661			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	13.7	12413367	4
top	17.407	191745	36921
end	25.25	28	96

Figure B-10 The GPC chromatograph of PS-G15/36 sheet at 6-month outdoor exposure.



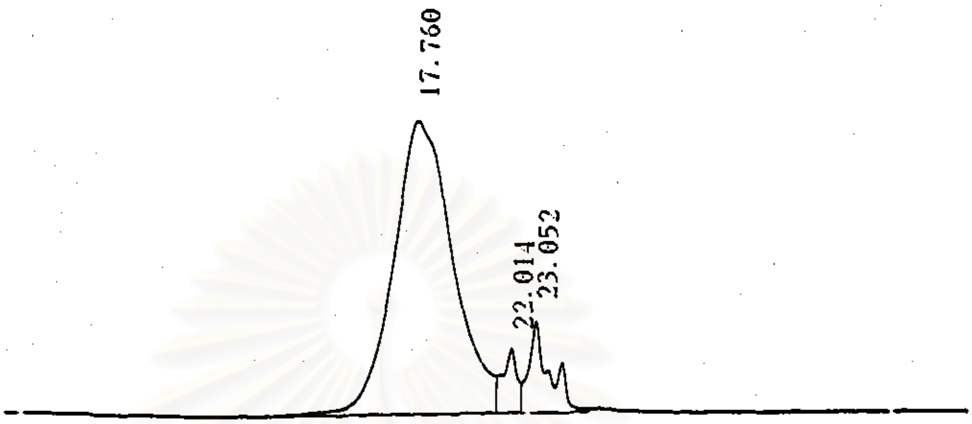
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	16.944	3084947	21093			92.7525
	2	22.061	119165	3886	V		3.5828
	3	23.040	121887	3984	V		3.6647
			....	....			......
	TOTAL		3325999	28963			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	14.05	8373127	2
top	16.944	322803	21093
end	23.9	129	523

Figure B-11 The GPC chromatograph of PS-G15/36 sheet at 100 kGy absorbed dose.



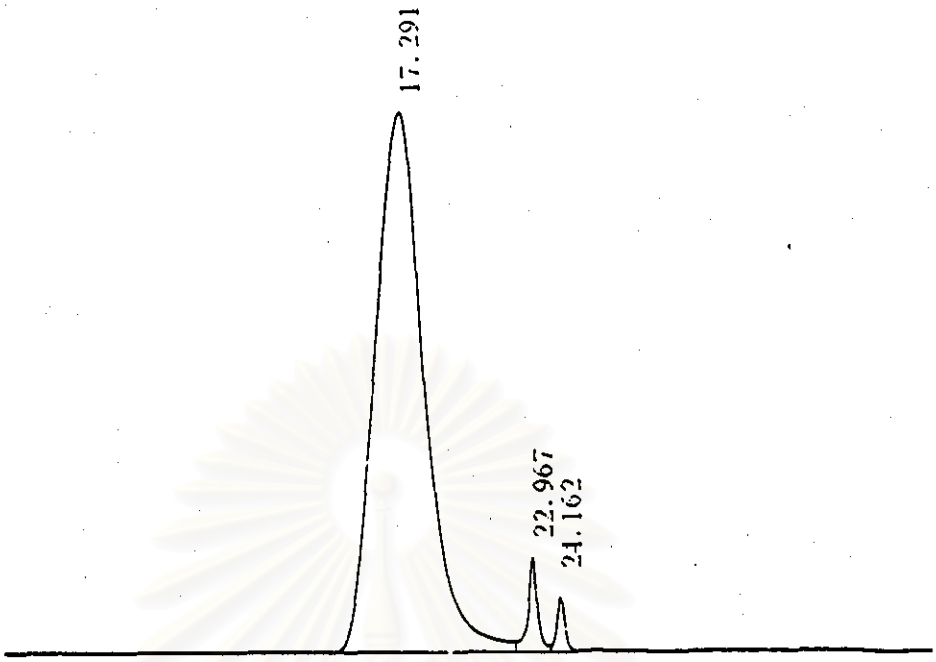
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.760	3224007	17557			86.2512
	2	22.014	173215	3749	V		4.634
	3	23.052	340707	5373	V		9.1148
			…………	……			……..
	TOTAL		3737928	26680			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	11.05	244695536	1
top	17.761	128853	17557
end	25.4	24	281

Figure B-12 The GPC chromatograph of PS-G15/36 sheet at 300 kGy absorbed dose.



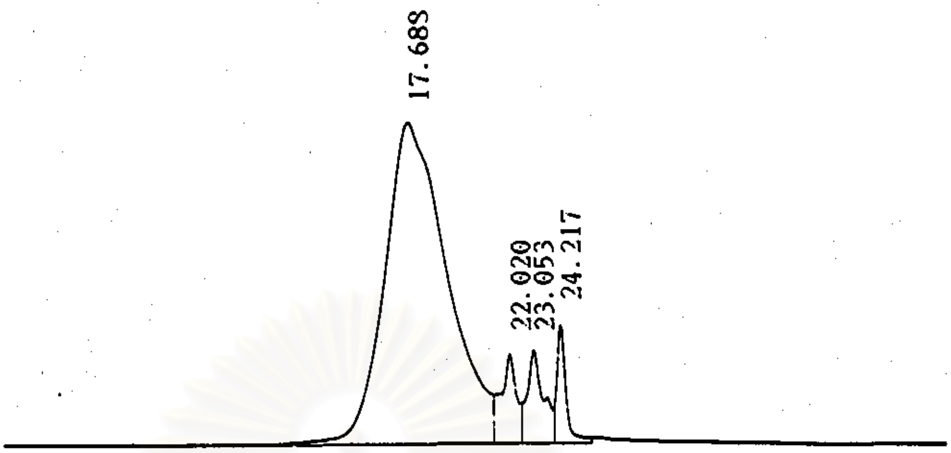
** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.291	19173404	128988			95.1729
	2	22.967	651897	21305	V		3.2359
	3	24.162	320555	12171	V		1.5912
			....	....			....
	TOTAL		20145854	162464			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	13.7	12413367	2
top	17.291	218474	128988
end	25.45	23	171

Figure B-13 The GPC chromatograph of PS-G15/36 sheet at 10-hour UV irradiation time.



** CALCULATION REPORT**

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	17.688	3636426	19203			83.6437
	2	22.020	248078	5221	V		5.7062
	3	23.053	274090	5359	V		6.3045
	4	24.217	188926	6892	V		4.3456
			....	....			....
	TOTAL		4347519	36675			100

TOTAL DATA CHANNEL 1

PEAK INFORMATION	TIME (min)	MOL. SIZE	HEIGHT
start	11.4	165052848	2
top	17.688	139776	19203
end	25.55	20	568

Figure B-14 The GPC chromatograph of PS-G15/36 sheet at 21-hour UV irradiation time.

VITA

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