



## Polymer Fractionation by Automated Laboratory System with Laser Optical Probe (L.A.F.P.)

Mustafa Tolay<sup>1\*</sup> , Cemil Koyunoğlu<sup>2</sup> , P. Cinquina<sup>3</sup>

<sup>1</sup>Tolay Energy Consulting, 19 Mayıs Mah. Halaskargazi Cad. Feza Apt. No: 192, D:8, Şişli, 34360, İstanbul, Turkey

<sup>2</sup>Energy Systems Engineering Department, Engineering Faculty, Cinarcik Road 5<sup>th</sup> km, Central Campus, Yalova University, 77200, Yalova, Turkey

<sup>3</sup>Istituto Guido Donegani, Enichem, Via G.Fauser, 4, 28100 Novara-Italia

**Abstract:** By examining the composition of copolymers and the distribution of their molecular weights, one can get an idea about their various properties. It is necessary to obtain homogeneous samples from fractions of different molecular weights of copolymers. Fractionation processes are quite difficult and time consuming. In this study, a type of ethylene-propylene copolymer was fractionated depending on molecular weight with a system based on laser turbidity measurement. The copolymer was dissolved in diphenylmethane at a certain temperature. The temperature of the system and the adjustment of other parameters are made with the developed computer-controlled system. When the temperature of the solution was lowered slowly and in a controlled manner, the separation of fractions with certain molecular weights could be achieved. The solution turbidity formed during the separation was measured and controlled by the developed laser system. Molecular weights, viscosities and IR analyses of the copolymer and its fractions were tried to find the properties of the fractions.

**Keywords:** Polymer fractionation, molecular distribution, laser probes, laboratory automation, batch chemical reactors.

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**\*Corresponding author. E-mail:** [drmtolay@libero.it](mailto:drmtolay@libero.it).

### INTRODUCTION

The ethylene-propylene copolymers, their derivatives, and similar polymers are among interesting elastomers both from the theoretical and commercial point of view. It is very well known that the physical-mechanical and application properties of copolymers are strongly dependent on their structure. Included in the structure are, generally, the molecular weights and their distributions, the average composition and its variations around the average value and, finally, the chain sequences and their microstructure. The prevailing influence of some of these, instead of others, can explain the conflicting results and conclusions drawn from

studies based average values of molecular weights and composition of different raw materials. The problem, therefore of separating homogeneous species concerning both the molecular weights and composition, is presently of great interest (1-4).

SEC chromatography has been recently useful in helping to solve problems in which some structural parameters overlap each other. Many years ago, the use of appropriate combinations of detectors has been a powerful tool in solving complicated molecular structures like polymer chain branching (5-8).

Where for homopolymers it is possible to obtain, in selected conditions, molecular weight distribution very close to real ones, the same may not be true for copolymers. It is necessary to take into account, possible compositional inhomogeneities that could influence the univocity of a correct calibration relationship between the retention volume and the molecular weight of eluted species. The same could be true concerning the concentration of molecular species if an RI detector is used. If the composition does not show variations over the whole range of molecular weight, the same assumption used for homopolymers can be applied also to the copolymers. However, this situation is unusual for most copolymers.

Otherwise, it is very important to choose a solvent which minimizes the  $dn/dc$  difference between the copolymers (5), in order to eliminate or to drastically reduce the influence of composition. Taking all these things into account, we tried to check the validity and reliability of some proposed relationships (9-11) for the copolymers under investigation.

For this reason, it has been necessary to prepare fractions which are homogeneous both in respect to molecular weight and composition to represent the real polymer distribution. In this study, a fractionation method is reported which separates the raw copolymer mainly as a function of its molecular weight mass. For this study, also a laser probe and an automated laboratory system (L.A.F.P.) are reported to developed for this polymer fractionation method was used (12-15).

## EXPERIMENTAL STUDIES

### Sample

The sample used in the experiment was a commercial (BUNA AP 301) ethylene-propylene copolymer (Table 1) from Chemische Werke Hüls Ag.

**Table 1:** Properties of BUNA AP 301 Copolymer.

$[\eta]$ (dL/g)	Mw	MWD	C <sub>3</sub> (%wt)	Mooney M <sub>L4</sub> (at 100 °C)
1.8	230,000	2.6	43.8	75

### Fractionation Process

Fractionation process was carried out using a single solvent at certain temperature ranges. The sample dissolved in the solvent at a certain temperature was separated into its fractions by slowly decreasing the solution temperature. The fractionation process was carried out in a jacketed fractionation device with automatic temperature control with a computer. Diphenylmethane was used as the

solvent and the polymer concentration was chosen as 1%. In order to prevent polymer degradation, 0.1% mixture of Irganox 1076 and Irganox 1010 was added to the polymer solution as a stabilizer. After the polymer solution to be fractionated was prepared, it was heated up to a maximum of 160 °C. No visible degradation was observed at this temperature. For the fractionation process, the temperature of the solution was lowered slowly, and according to the experimental plan, the fractions were set at the temperatures given in Table 2. A special thermostatic system (L.A.P.F.-Laboratorio Automatico per Il Frazionamento Polymer) developed for the fractionation process and controlled by a computer was used (Figure 1) (12-15). The solution turbidity formed during the separation of the fractions was measured and controlled with the developed laser probe (Figure 2) (12-15). Samples separated at each temperature range were weighed and stored for analysis. After each step of the separation process, the mixing process was continued while the temperature of the solution was lowered. Mixing was stopped to perform separation only after the desired temperature was reached. The fraction number was determined according to the molecular weight distribution of the polymer and the selected temperature range. During the whole fractionation process, it was worked in a nitrogen gas atmosphere.

### Viscosity Measurements

The actual viscosity  $[\eta]$  values of the starting crude copolymer and its fractions were measured with o-dichlorobenzene at 135 °C. Actual viscosities are the viscosity values measured at four different concentrations,  $h_{spec}/C$  was found by extrapolation to zero concentration. Measurements were made with a Desreux-Bischoff capillary viscometer (16).

### SEC Analysis

Average molecular weights of the starting crude polymer and its fractions and their distributions were determined by gel permeation chromatography method. Four PL GEL 10  $\mu$  (103 - 104 - 105 - 106 Å) mounted Waters 150-C ALC/GPC instruments were used with a differential refractive index detector. Analyses were performed at 135 °C using o-dichlorobenzene. Thus, the  $dn/dc$  ratio is minimized when EPR copolymers are used (10). The calibration curve was made according to the Mark-Houwink equations proposed by Benoit et al. (17).

### IR Analysis

The composition of the starting crude copolymer and its fractions was determined with the PERKIN-ELMER 1800 Mod.FTIR instrument. 2723  $cm^{-1}$  absorption band ( $-CH_3$  symmetrical slope) was used as the calibration curve (Tables 1, 2, and 3).

### Automated Laboratory System

L.A.F.P. developed for the fractionation process and controlled by a computer was used (Figure 1). The Automated Laboratory System is also used for the automatic execution of batch or semi-batch chemical reactions. Automated Laboratory System is an automated lab reactor whereby a constant temperature is maintained within a system and the heat flux to or from the system is measured by computer control. The reactor is equipped with precise and rapid temperature control. The agitator motor that drives the standard agitators (anchor agitator, propeller, or turbine agitator, etc.) has an adjustable speed control. In addition, other process parameters such as dosing, pH of the reaction medium, pressure, etc. are measured and controlled (Figure 1) (11-14).

### Laser Optical Probe System

With the computer-controlled laser probe, which measures and controls the solution turbidity that occurs during fractionation of polymers, the efficient operation of the system has been increased and homogeneous fractions have been obtained. To enable continuous detection of solution concentration without stopping the operation of the equipment. A cylindrical probe 3 is provided with a slit portion 3' to which lenses 4 and 4' are attached. When the probe 3 is charged, the inside of the slit portion 3' is filled with the solution. Then, the beam  $f$  emitted from the laser 21 is split into beams  $f$  2 and  $f$  3. The beam  $f$  3 then becomes beams  $f$  4 to  $f$  9 and is reflected by the reflecting device 7 and becomes a beam  $f$  10 and merges with the beam  $f$  2. Then, the differential amplifier 10 is connected via the photosensor 8 and the current / voltage converter 9. The signal 11 representing the solution concentration is output by being input to the input terminal and compared with the reference signal 12 (Figure 2) (14).

## RESULTS

If a copolymer dissolved in a single solvent (high temperature-resistant organic solvent) is fractionated due to a temperature difference, the fractionation process occurs by the effects between the polymer and the solvent. The separation process depends on the molecular weight of the copolymer, its composition, or a combination thereof. The

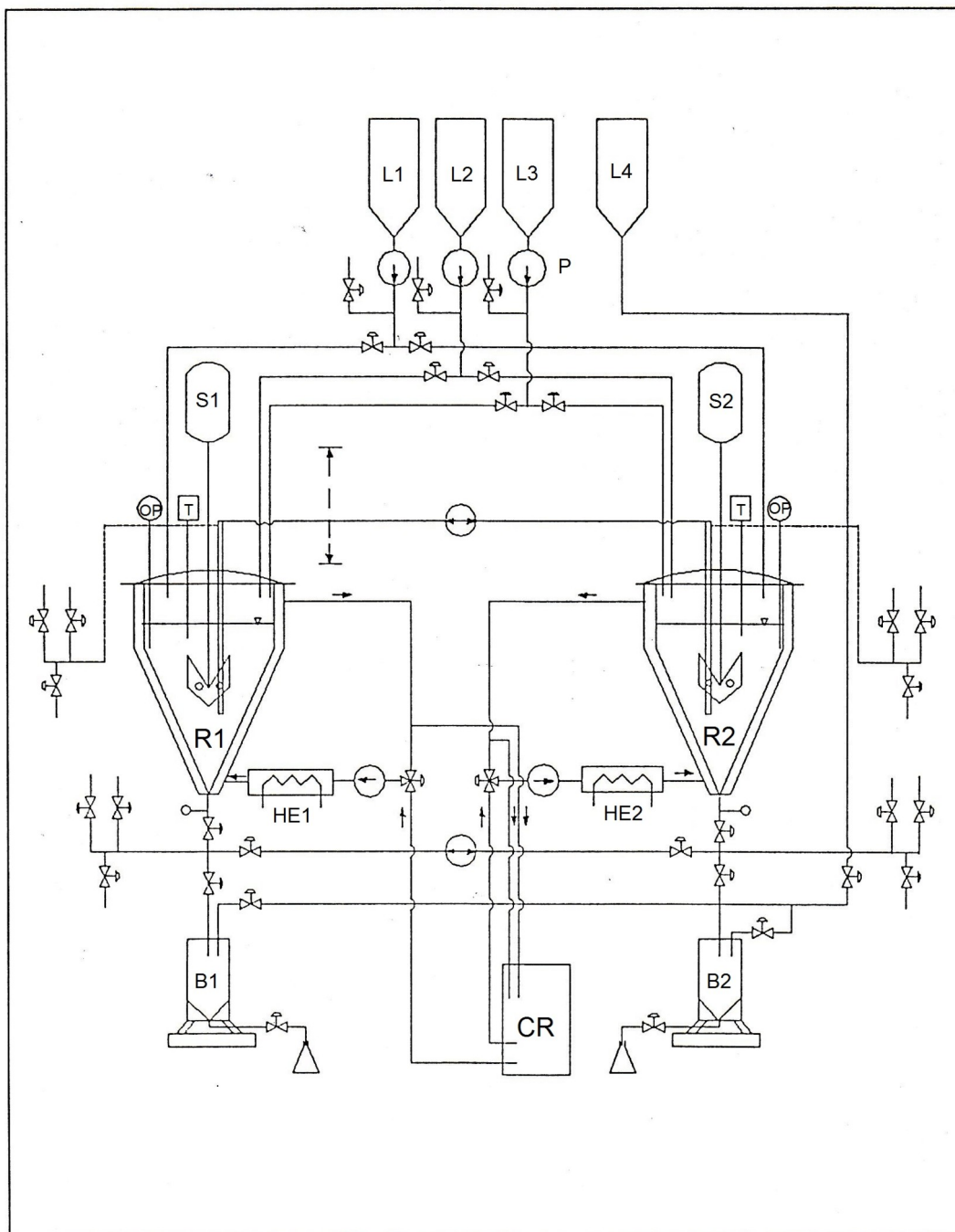
distribution of copolymer molecules in the two equilibrium phases is expressed by the following equation (11):

$$V' / V = \exp [P(\sigma - Kw)] \quad (1)$$

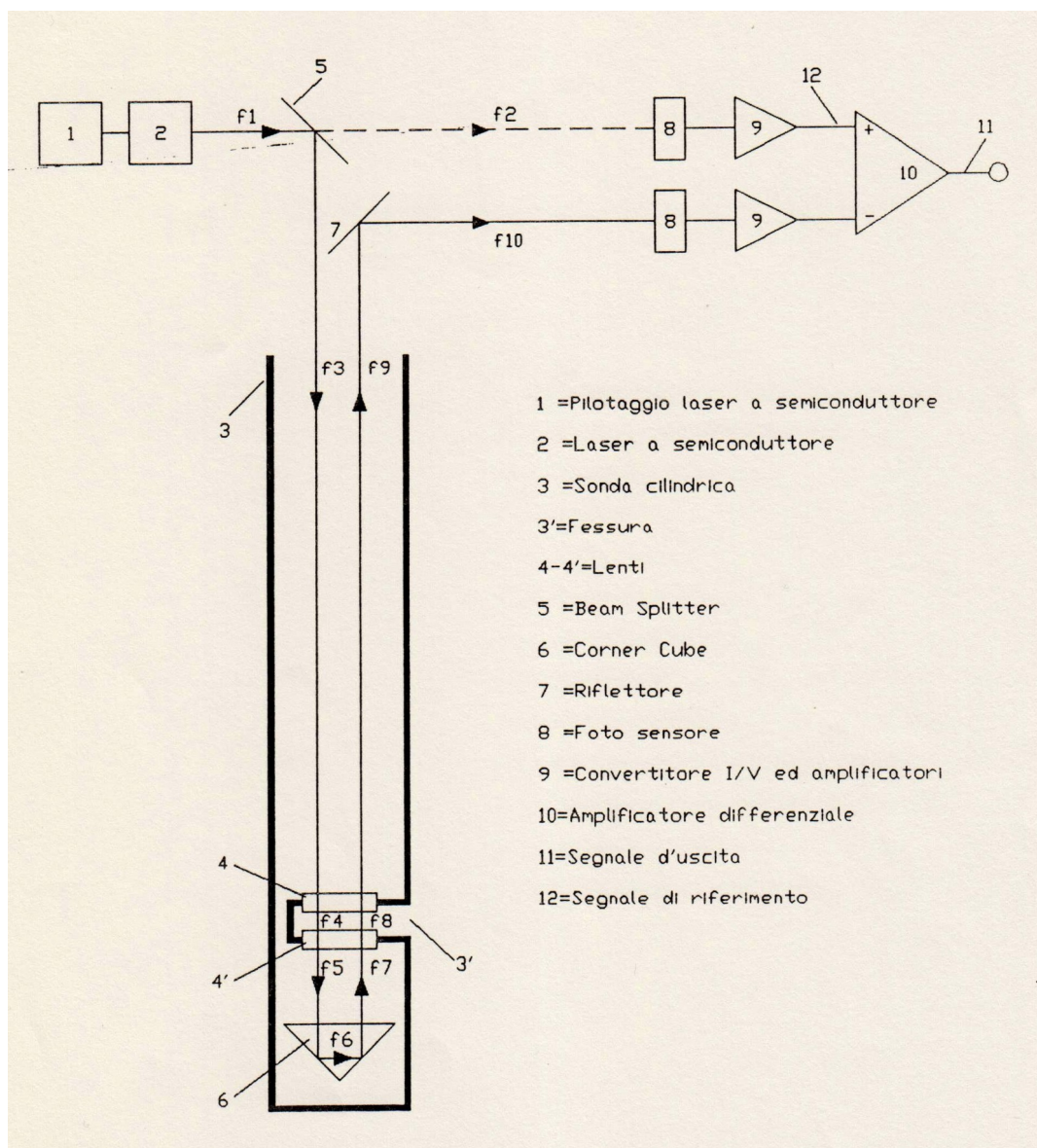
Here,  $V'$  and  $V$  define the volume fraction of a single component that is in solution and decomposes sequentially.  $P$  indicates the degree of polymerization,  $\sigma$  the fractionation parameter, and  $w$  the polymer composition. The  $K$  value for a single solvent system is defined as:

$$K = (V' - V) (X_A - X_B) \quad (2)$$

Here, the terms  $X_A$  and  $X_B$  refer to the interaction between the A and B copolymer units and the solvent. If  $X_A = X_B$ , then the  $K$  value will naturally be zero. The fractionation process is completely dependent on molecular weight (1-4). Composition and MWD values [Molecular weight distribution of polymers; degree of polydispersion ( $M_w/M_n$ )] of BUNA AP 301 copolymer and its fractions are given in Table 2. The molecular weight distribution of the fractions obtained in this study was evaluated according to the Tung and Scholte methods given in the literature (9,10). Table 3 shows the molecular weight distributions of the copolymer fractions obtained as a result of fractionation and their evaluation according to Tung and Scholte methods. In the evaluation made according to the Tung method, the molecular weight distribution is mostly in the form of Gaussian. In contrast, the Scholte assessment is more limited than the Tung assessment since linear macromolecules with short side chains are considered. However, as can be seen in Table 3, the results of both evaluations are close to each other with a difference of  $\pm 10\%$ . When the molecular weight distributions, MWD, viscosity values and other evaluations are examined together, it is seen that this fractionation system (L.A.F.P.) developed is quite effective. Especially with the computer-controlled laser probe, which measures and controls the solution turbidity that occurs during fractionation, the efficient operation of the system has been increased and homogeneous fractions have been obtained. With this method, a large amount of fractions with different molecular weights required for copolymer studies are obtained.



**Figure 1.** Computer-Controlled Automatic Laboratory System Used in Polymer Fractionation (L.A.F.P.), European Patent No: 911044370.1, 20.03.1991 [12,13,14,15] (R: Reactors for Polymer Fractionations, L: Polymer Solutions Sample Tanks, CR: Reactor Cooling and Heating System, HE: Heat Exchangers for Reactors, B: Samples Collection Tanks and Balance, S: Reactor Stirrers, T: Thermometers, OP: Laser Probe Systems).



**Figure 2.** Laser Probe System with Computer Controlled Automatic Laboratory System Used in Polymer Fractionation (L.A.F.P.), European Patent No: 911044370.1, 20.03.1991 (12-15).

**Table 2:** Properties of Fractions of BUNA AP 301 Copolymer Obtained From Diphenylmethane Solution.

No	(°C)	Fraction	(%wt)	(dL/g)
1	120	0.2000	2.5	42.6
2	117	0.2033	2.3	44.4
3	114	0.0656	1.6	43.4
4	112	0.1092	1.8	43.8
5	110	0.0687	1.6	44.0
6	106	0.0862	1.3	44.0
7	95	0.1501	1.4	43.3
8	90	0.0479	1.4	42.9
9	80	0.0231	1.6	42.2
10	70	0.0251	1.5	44.2
11	25	0.0208	2.5	n.d.
BUNA AP 301	-	-	2.6	43.8

**Table 3:** Analysis Results of Samples Obtained by Fractionation Evaluation

Fraction No	M <sub>w</sub> (PE)	M <sub>w</sub> (PP)	C <sub>3</sub> (% wt)	M <sub>w</sub> (Tung)	M <sub>w</sub> (Scholte)
1	305,000	556,000	42.6	394,000	356,000
2	217,000	350,000	44.4	269,000	255,000
3	205,000	334,000	43.4	254,000	240,000
4	167,000	271,000	43.8	207,000	196,000
5	149,000	240,000	44.0	183,000	174,000
6	131,000	211,000	44.0	161,000	153,000
7	97,000	156,000	43.3	119,000	114,000
8	70,000	112,000	42.9	85,000	82,000
9	57,000	92,000	42.2	70,000	67,000
10	38,000	60,000	44.2	46,000	44,000
11	19,000	31,000	n.d.	24,000	22,000
BUNA AP 301	187,000	302,000	43.8	230,000	220,000

n.d. : not measured, MWD: Molecular weight distribution of polymers; degree of polydispersion (Mw/Mn), Mw: average molecular weight, Mn: number average molecular weight. %C<sub>3</sub> : percent polypropylene content (from IR analysis). [η] : the actual viscosity of the polymer.

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