are widely used in temporary therapeutic applications such as wound closure, tissue regeneration and sutures [15], which motivates the necessity to investigate different properties of such an important blend. PMMA/PCL microheterogeneous beads of controlled size and distribution were synthesized by Abraham *et al.* [16] using suspension polymerization beginning from methyl methacrylate (MMA) monomer and PCL. The low compatibility between PMMA and PCL was evidenced through this research work. In recent years, supercritical fluid approach has been introduced as a safe modern technique to provide PMMA/PCL blends which allows free-contaminant structures to obtain [15, 17]. Since solvent casting offers one of the well-known methods to prepare polymer blends [1], it seems indispensable to survey the influence of solvent properties on the miscibility behavior of PMMA/PCL blends.

Several analytical methods including spectroscopy [2-4], viscosimetry [5], microscopy [5, 18, 19], thermal analysis [2-5, 20-22] and inverse gas chromatography [23-25] have been employed to characterize polymer-polymer miscibility. Among these analytical methods differential scanning calorimetry (DSC) is one of the most widely used techniques for evaluating miscibility and phase behavior [1].

In this paper, PMMA and PCL as well as blends of them (50/50 wt%) were prepared in three different solvents, dichloromethane (DCM), tetrahydrofuran (THF) and toluene (TOL), to form 18 wt% polymer solutions. The solutions were allowed to separate into two phases. To characterize the composition of each phase, thermal characteristics of films cast from both phases i.e., PMMA-rich and PCL-rich phases were evaluated by differential scanning calorimetry (DSC) and dynamic mechanical analyzer (DMA). The effect of solvent on the miscibility of both polymers was analyzed through the thermal events such as glass transition temperature and enthalpies of melting.

II. EXPERIMENTAL

A. *Materials*

Poly (methyl methacrylate) (PMMA) was synthesized with the number average molecular weight M_n=75000 g/mol^{-1} and weight average molecular weight M_w=84000 g/mol^{-1}. Molecular weights were measured by gel permeation chromatography (GPCV 2000- Waters, USA) using a calibration curve of polystyrene standards. Poly(ε-caprolactone) (PCL) (donated by hzg) was supplied as CAPA 6800 by Solvay in pellet form. The PCL had a weight average molecular weight of 120,000 ± 2000 g mol^{-1} and a number average molecular weight of 69,000± 1500 g mol^{-1}. Before making solutions, the PMMA and PCL were dried at temperatures of 110 °C and 30 °C, respectively, in a vacuumed oven for 24 h. Solvents including dichloromethane (DCM), tetrahydrofuran (THF) and toluene (TOL) were purchased from Merck, Germany and used without further purification.

B. *Sample preparation*

PMMA/PCL with the weight ratio of 50/50 was dissolved in dichloromethane (DCM), tetrahydrofuran (THF) and toluene (TOL) at room temperature under gentle stirring until a solution with a polymer concentration of 18 wt% was obtained. The obtained solutions were kept for 48 hours at room temperature to reach an equilibrium state. The solutions were separated into two equilibrium phases if they were unstable mixtures. In the case of demixed solutions, as demonstrated in Fig. 1, the upper (PCL-rich) and the beneath (PMMA-rich) phase of demixed solutions were cast with an adjustable clearance applicator (BYK Gardner) with a thickness of 200 μm and then placed into the atmospheric condition for evaporating the solvent. To remove the residual solvent the cast films were dried for 48 hours under vacuum at 30 °C.

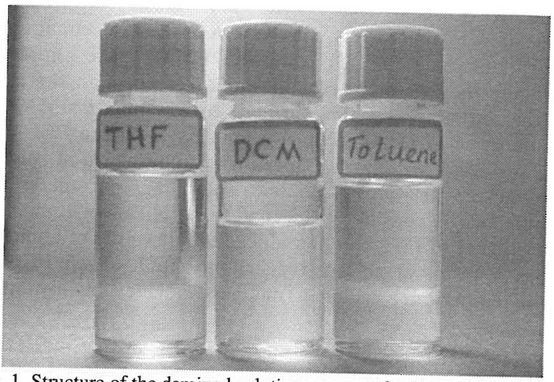

Fig. 1. Structure of the demixed solutions separated to two phases.

C. *Thermal analysis*

Thermal analysis was performed using a differential scanning calorimeter (DSC), TA Instruments, DSC 2010. Samples with approximately similar mass (4.50 mg) were heated from 0 °C to 180 °C at scan rate of 20 °C/min. Samples were annealed at this temperature (180 °C) for 5 min to completely remove the morphological history. Then, the annealed samples cooled down at the scan rate of 5 °C/min to 0 °C and after that heated again up with the same procedure as the first heating.

Viscoelastic properties of the blends were measured in the temperature range of 25-180 °C by dynamic mechanical analysis (DMA), TA Instruments, DMA 2980. Dynamical experiments were carried out using an extensional method in a film tension clamp. The temperature scan rate was fixed at 2 °C/min and the other procedure parameters were the frequency 1 Hz, the force track 120%, and amplitude 0.1% for all samples.

III. RESULTS AND DISCUSSION

A. *PCL-rich phase*

Figure 2 presents the first cut of DSC thermograph of samples quenched from PCL-rich phase of PMMA/PCL solution blends for two runs of heating: first heating and second heating. These samples were labeled by rPCLDCM, rPCLTHF, and rPCLTOL, referring to preparation in different solvents, i.e. DCM, THF, and TOL, respectively. For comparison, the neat PCL was also dissolved in different solvents and then treated as similar to PCL-rich phases, labeled by nPCLDCM, nPCLTHF, and nPCLTOL. From Figure 2 it becomes clear that the sign of neat PCL is strongly appeared in the thermographs indicating crystalline phase domain formed during the solvent evaporation, however the melting point and degree of crystallinity in various samples are different. Notwithstanding the variation in the melting behavior of PCL which has been influenced by solvent casting process, they behave similar in the second heating run. The appearance of melting peak in samples obtained from PCL-rich phase of blends is an indication of demixing during solvent evaporation. The presence of the other phase containing PMMA with high concentration will be a subject to investigate in following.

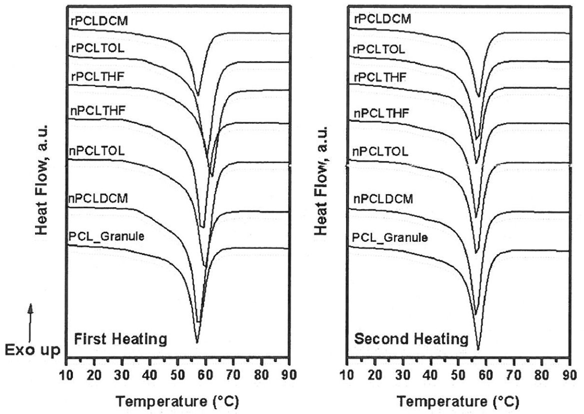

Fig. 2. DSC thermographs obtained during first and second heating run in PCL melting region of PCL granule, neat PCL as well as PCL-rich phases in different solvents.

Figure 3 shows the second cut of DSC thermograph of samples quenched from PCL-rich phase of PMMA/PCL solution blends for two runs of heating: first heating and second heating, to probe the presence of PMMA by its glass transition. As seen in Figure 3, there is an obviously thermal event at temperature of about 112 °C for the samples of rPCLTHF and rPCLDCM, assigning the glass transition of PMMA, while nothing is observed for rPCLTOL. After removing thermal history of the samples, the glass transition of PMMA for all samples is observed in the second heating at temperature between 113-114 °C.

Thermal properties of samples including melting temperature, enthalpy of fusion, and glass transition temperature were listed in Table I. Note that, estimation of glass transition temperature for PMMA was carried out from the midpoint of the DSC curve in the desired temperature region.

As evidenced in Figure 2 and Table I, in the case of films cast from neat PCL in different solvents (nPCLTHF, nPCLTOL and nPCLDCM), melting temperature as well as enthalpies of melting of PCL is slightly influenced by the casting solvent. Furthermore, enthalpies of melting of these samples are relatively more than that of PCL granule (gPCL). So, it can be said that solvents caused to more crystallinity for PCL with respect to its granule. This phenomenon could be ascribed to the solvent and polymer chains interaction.

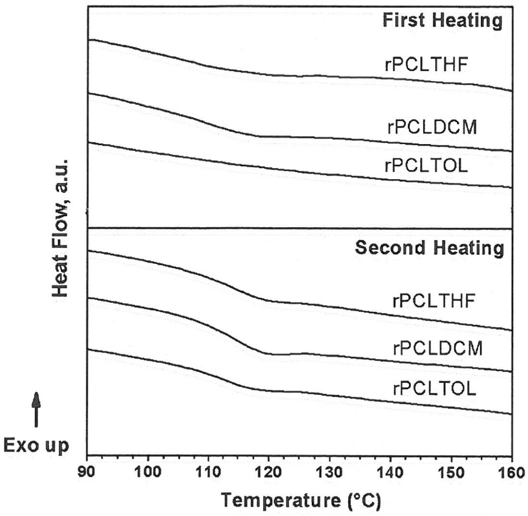

Fig. 3. DSC thermographs obtained during first and second heating run in PMMA glass transition region of PCL-rich phases in different solvents.

DCM and THF may be considered as good solvents for PCL, leading the polymer chains of PCL to expand themselves in the solutions to expose utmost part in contact with the solvent molecules. It makes the polymer chains more susceptible to crystallize. In the case of toluene, it seems the weak interaction of PCL chains with this solvent, causes to contraction of PCL chains and therefore reduce the crystallinity comparable to PCL granule. This claim regarding solvent effect on crystallinity of PCL chains, could be verified by calorimetric data obtained from second heating process as shown in Figure 2

TABLE I

THERMAL ANALYSIS DATA OBTAINED AFTER FIRST AND SECOND HEATING RUN OF PCL GRANULE, PURE PCL AS WELL AS PCL-RICH PHASES IN DIFFERENT SOLVENTS

Sample	First Heating			Second Heating		
	PCL heat of fusion (J/g)	PCL melting point (°C)	PMMA glass transition (°C)	PCL heat of fusion (J/g)	PCL melting point (°C)	PMMA glass transition (°C)
gPCL	55.0	57.0	-	55.1	57.0	-
rPCLDCM	34.7	56.8	111	34.5	56.7	115
rPCLTHF	44.9	59.6	112	36.3	56.4	114
rPCLTOL	53.7	59.9	-	42.8	56.4	114
nPCLDCM	63.6	57.5	-	54.2	56.3	-
nPCLTHF	62.8	58.5	-	48.7	56.2	-
nPCLTOL	56.7	59.6	-	48.4	56.4	-

and Table I where the enthalpies of melting for neat PCL cast from various solvents are smaller than that of PCL granule. The arrangement of polymer chains as a result of polymer-solvent interaction will be disordered after first heating run and PCL chain conformation is transformed to that before solvent casting process which is less prone to crystallize. So it can be considered that solvent play a prominent role in crystallinity of PCL molecules which is evidenced from the great differences between the enthalpies of melting correspond to various pure PCL solutions in the first and second heating runs. The interaction of PCL with used solvents will be further examined later.

Exploring the heat of fusion of the samples cast from PCL-rich phase, given in Table I, shows that the highest value is obtained by sample rPCLTOL while the lowest value is obtained for sample rPCLDCM. It seems that the solvent quality causes the equilibrium composition of PCL-rich phase in different solvents to change, meaning that the lower the enthalpy of fusion of PCL, the higher the concentration of PMMA dissolved in PCL-rich phase. In the case of toluene, the weaker interaction with PMMA chains and probably relatively favorable interaction with PCL lead to make a PCL-rich phase with lower PMMA content, corresponding to higher PCL heat of fusion, than other solvents. On the other hand, as reported in Table I, different enthalpies of fusion are obtained for PCL treated in various solvents as well as PCL granule, ascribing that the interaction between solvent and polymer segments acts as an affecting factor to vary the crystallinity of PCL. Such observable verity should be considered to analyze the samples obtained from PCL-rich phase of the blend. To remove the effect of solvent on evolution of structure, the thermal characteristics of samples were investigated on the basis of second heating run. The results approve our claim regarding the ability of DCM for raising the PMMA content of PCL-rich phase in comparison with other solvents. Therefore, it can be figured out that enthalpies of PCL in the PCL/PMMA solution blend result in a series of decreasing solvent power to mix two incompatible polymers (PMMA and PCL) in PCL-rich phase according to DCM>THF>TOL.

According to the results, PCL-rich phase in various solvents show three different phases, i.e. neat PCL, pure PMMA and mixed PCL/PMMA phases when it is undergoing solvent evaporation. Therefore, PMMA in PCL-rich phase may exist in two different states, i.e. neat PMMA domain and mixed with PCL. In mixed PCL/PMMA domain, PMMA chains act as a glassy polymer which restricts the PCL crystallization. Generally, the presence of a glassy component in a solution of a semi-crystalline polymer reduces the crystallization [26]. The presence of neat PMMA chains could be distinguished from its glass transition temperature of PMMA, as shown in Figure 3.

B. PMMA-rich phase

Figure 4 represents the DSC thermograph of samples quenched from PMMA-rich phase of PMMA/PCL solution blends for two runs of heating: first heating and second heating. These samples were labeled by rPMMADCM, rPMMATHF, and rPMMATOL, referring to preparation in different solvents, i.e. DCM, THF, and TOL, respectively. For comparison, the neat PMMA was also dissolved in different solvents and then treated as similar to PMMA-rich phases, labeled by nPMMADCM, nPMMATHF, and nPMMATOL.

From Figure 4 it becomes clear that the quality of solvents varies the composition of components in equilibrium state, affecting thermal behavior of sample. The glass transition of rPMMATOL is lowest while which of rPMMADCM is highest, meaning that more PCL is dissolved into the PMMA-rich phase when toluene is used as solvent than DCM. Such a sorting can be confirmed by probing the PCL heat of fusion in the second heating stage appeared around 54 °C, assigning the PCL crystal domains. These enthalpies result in a series of decreasing solvent power to mix two incompatible polymers (PMMA and PCL) in PMMA-rich phase according to TOL>THF>DCM.

After running the first heating and isothermal standing at 180 °C for 5 minutes, all three samples rPMMATOL, rPMMATHF, and rPMMADCM show approximately the same temperature of 108 °C for glass to rubber transition, as expected. Comparing with granule of PMMA, the T_g of PMMA is observed at 117 °C, which is about 9 °C higher than PMMA/PCL blend.

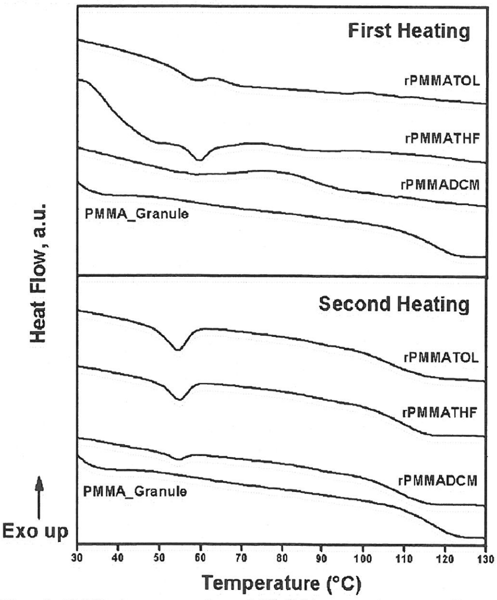

Fig. 4. DSC thermographs of PMMA granule as well as PMMA-rich phases in different solvents during first and second heating runs.

To estimate the composition dependence of T_g for the blends, the Fox equation [9] can be employed.

$$\frac{1}{T_{g,m}} = \frac{\omega_1}{T_{g,1}} + \frac{\omega_2}{T_{g,2}} \qquad (1)$$

where ω_i and $T_{g,i}$ are weight fraction and glass transition temperature of component i, and 1 and 2 index the PMMA and PCL, respectively.

According to the Fox equation, it is possible to estimate

TABLE II

THERMAL ANALYSIS DATA OBTAINED AFTER FIRST AND SECOND HEATING RUN OF PMMA GRANULE, PURE PMMA AS WELL AS PMMA-RICH PHASES IN DIFFERENT SOLVENTS

Sample	First Heating			Second Heating		
	PCL heat of fusion (J/g)	PCL melting point (°C)	PMMA glass transition (°C)	PCL heat of fusion (J/g)	PCL melting point (°C)	PMMA glass transition (°C)
gPMMA			117			117
rPMMADCM			88	0.5	54.2	109
rPMMATHF	1.2	59.7	79	1.7	54.5	110
rPMMATOL			54	2.3	54.4	106
nPMMATHF			82			106
nPMMATOL			78			108
nPMMADCM			97			109

the capability of PCL to dissolve into PMMA-rich phase in a binary mixture. Considering T_g of PMMA and PCL equal to 117 °C and -60 °C respectively and also $\omega_1 + \omega_2 = 1$, the calculated composition of blend, based on equation 1, will be $\omega_1 = 97.2$ and $\omega_2 = 2.8\,\text{wt\%}$ for $T_{g,m} = 108\ ^{\circ}\text{C}$ (obtained from second heating process). It means that, the maximum value of PCL which is able to dissolve into the PMMA is 2.8 wt%.

Thermal properties of samples including melting temperature, enthalpy of fusion, and glass transition temperature for PMMA-rich phase as well as neat PMMA were listed in Table II.

As listed in Table II, the glass transition temperature of PMMA has been greatly influenced by the quality of solvent. T_g of the PMMA granule is about 117 °C whilst which of nPMMATOL, nPMMATHF, and nPMMADCM are appeared in lower temperatures. This observation could be interpreted by the fact that introduction of solvents in the polymer structure leads to an increase in the free volume of the polymer system and thus enhances the mobility of polymer chains [27] required for glass transition to be occurred. In addition, the amount of glass transition depression varies with the type of solvent used in the casting process which originates from the interactions of solvent with polymer. According to Table II, the values of T_g for nPMMATOL and rPMMATOL are 78.5 °C and 54.7 °C, respectively. As clearly observed by enthalpy of fusion, the presence of PCL in rPMMATOL sample leads to depression of T_g to a great extent, acting as a plasticizer. Such justification can be generalized to the other samples quenched from PMMA-lean and PMMA-rich phase in different solvents (i.e. THF and DCM).

To further investigation of the glass transition region of PMMA, viscoelastic properties of films cast from PMMA-rich phases in different solvents (i.e. rPMMADCM, rPMMATOL and rPMMATHF) were measured by DMA experiment. The variation of loss modulus against temperature for above-mentioned samples has been depicted in Figure 5. The temperature at which loss modulus is largest value corresponds to glass transition temperature. This temperature for samples rPMMADCM, rPMMATOL and rPMMATHF has been measured to be 80, 54 and 61 °C, respectively.

Comparing data obtained from DMA and DSC experiments (listed in Tables II), it can be realized that there is complete agreement between DMA and DSC results. Small differences, of course, may be attributed to principles of these techniques. This agreement demonstrates a tremendous reduction in glass transition temperature of PMMA as a result of plasticization created by solvent-induced miscibility which is of great commercial and scientific interest. As previously discussed, the most reduction in PMMA's T_g has been induced by TOL which has the most unfavorable interaction with PMMA. This extraordinary behavior will be discussed in the next section.

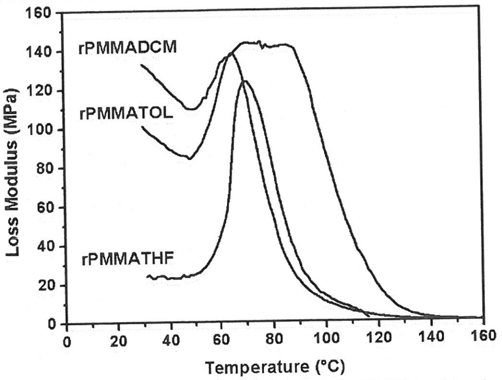

Fig. 5. Loss modulus curves of films cast from PMMA-rich phases in different solvents.

According to the obtained thermographs from second heating, it is obviously distinguished that there are two thermal events; firstly an endothermic peak is appeared, assigning the PCL accumulates in a pure domain and secondly a glass transition which is lower than glass transition of neat PMMA, assigning the PCL is partially mixed with PMMA in a mixture domain. Dissimilar behavior is observed for the samples in first heating thermographs in which the history of structure affected by quality of solvent is clarified in the first heating. As understood, the solvent THF could dissolve the PCL in PMMA-rich phase more than the solvent DCM. This is clearly verified by second heating thermographs in the PCL melting region (Figure 4). But in the first heating thermographs, a small endothermic event is appeared for the sample quenched from THF solution while nothing happens for which of DCM solution. This is described by effect of casting condition, meaning that the solvent evaporation causes to concentrate the solution and then leads to phase separation in the case of THF solution.

TABLE III
PARTITIONING CHARACTERISTICS OF PMMA/PCL BLEND SOLUTIONS

Polymer blend solution	**PMMA-rich phase**		**PCL-rich phase**	
	Partial volume	Weight fraction of solvent	Partial volume	Weight fraction of solvent
PMMA/PCL/DCM	0.4	0.73	0.6	0.79
PMMA/PCL/THF	0.32	o.71	0.68	0.79
PMMA/PCL/TOL	0.32	0.7	0.68	0.83

Nevertheless the results are verified in a series of decreasing solvent power according to TOL>THF>DCM.

C. Miscibility analysis

In the literature, several studies show that miscibility of two polymers is strongly influenced by solvent [9-14]. Here we experienced such effect by PMMA/PCL solution blend in three different solvents, dichloromethane, tetrahydrofuran, and toluene. As discussed in earlier sections, PMMA/PCL blend by ratio of 1:1 (wt/wt) is going to separate into two phases in all three solvents. However as shown in Figure 1, the volume of two phases is not equal; meaning that the molar free energy of phases varies when the quality of solvent changes. Besides, different compositions are also formed in separated phases by introducing the different quality of solvents. From analyzing the PCL- and PMMA-rich phases of DCM, THF, and TOL solutions, it has been recognized that the quality of solvent in each phases differs from the other. In the other word, the solvent behaves differently in each phase, according to the following state:

- PCL-rich phase: decreasing solvent mixing power according to DCM>THF>TOL
- PMMA-rich phase: decreasing solvent mixing power according to TOL>THF>DCM

As previously discussed, DCM could dissolve more PMMA in PCL-rich phase than other solvents. It means that DCM acts as a better solvent for interacting with PMMA in which it causes more PMMA chains to accumulate in the PCL-rich phase. While a weak interaction of TOL with PMMA leads to lower dissolution of PMMA in rPCLTOL phase than that of PMMA in rPCLDCM phase. THF acts as an intermediate between two extremes, i.e. DCM and TOL.

Volume of separated phases can be considered as another interesting point. As shown in Figure 1, it is clearly recognized that the volume of the separated phases for a given sample is not equal to each others in which this is observed for all three solvents, in spite of using the same ratio of PMMA/PCL (50:50) to make solutions of 18 wt%. Calculated partial volume of phases and also weight fraction of solvent in each phase are listed in Table III. In PMMA-rich phase, changing the solvent according to the series of TOL>THF>DCM, the volume fraction of solvent is increased, while in PCL-rich phase the observation is overturn, i.e. DCM>THF>TOL.

To integrate the aforementioned results, it can be concluded that, the TOL has not only been able to dissolve more PCL in PMMA-rich phase but it also makes a higher concentration of polymer blend solution (about 30 wt%) in the PMMA-rich phase. In contrast with TOL, THF and especially DCM make a lower concentration of polymer blend solution (29 wt% and 27 wt%, respectively) in case of PMMA-rich phase.

From Table III it is obvious that partitioning of solvent between two coexisting phases (PCL-rich and PMMA-rich) can be controlled by type of polymer which affects the solvent-polymer interaction. A good interaction between solvent and polymer raises solvent molecules around the polymer chains and makes the solution more diluted. In contrast, unfavorable solvent-polymer interaction reduces the number of solvent molecules around the polymer chains which is accompanied by incrementing polymer concentration.

D. Thermodynamic description

In this study, Hansen solubility parameters have been regarded as an appropriate criterion to investigate solvent-polymer interactions. Hansen solubility parameters of polymers and solvents are listed in Table IV.

TABLE IV
SPECIFICATIONS OF APPLIED SOLVENTS AND POLYMERS [28, 29]

Material	δ_d $MPa^{1/2}$	δ_p $MPa^{1/2}$	δ_h $MPa^{1/2}$	δ_t $MPa^{1/2}$	boiling point (°C)
DCM	17.0	7.3	7.1	19.8	40
THF	16.8	5.7	8.0	19.5	66
Toluene	18.0	1.4	2.0	18.2	111
PMMA	18.6	10.5	7.5	22.7	------
PCL	17.7	6.2	7.8	20.31	------

δ_t : total solubility parameter $\left(\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2\right)$, δ_d = dispersive contribution, δ_p = polar contribution, δ_h = hydrogen bonding contribution

To evaluate the effectiveness of used solvents (DCM, THF and TOL) to dissolve polymers of interest, i.e. PMMA and PCL, the distance (D) between solvent (S) and polymer (P) in the “Hansen solubility space” was calculated using Equation 2 applied by Bordes *et al.* [29]. Results have been reported in Table V.

$$D = (4(\delta_{ds} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2)^{0.5} \tag{2}$$

The concept of D value could be interpreted by the fact that a lower value denotes to more affinity of solvent to a given solute. In other words, all solvents dissolving the polymer, form a solubility sphere whose center is localized by that polymer. The more values of D denotes to lower compatibility between solvent and polymer [29].

Regarding data listed in Table V, the highest D value belongs to solutions of TOL, meaning an unfavorable interaction between TOL and both PCL and PMMA. But PCL compared to PMMA displays considerably smaller value for D denoting that affinity of TOL toward PCL is more than PMMA. It means although TOL is not categorized as a good solvent for PCL, but it is preferentially more tending to selectively interact with PCL rather than PMMA. This selectivity acts as a driving force to dilute PCL-rich phase and concentrate the PMMA-rich phase at equilibrium. The reduction of PMMA in rPCLTOL sample is another result of this selectivity feature which is distinguishable from PCL heat of fusion

TABLE V
CALCULATED DISTANCE (D) BETWEEN USED SOLVENTS AND POLYMERS IN THE "HANSEN SOLUBILITY SPACE"

Sample	PCL-THF	PCL-Toluene	PCL-DCM	PMMA-THF	PMMA-Toluene	PMMA-DCM
D	1.88	7.55	1.91	6.02	10.70	4.54

(Table I).

According to Table V, both DCM and THF can be considered as good solvents for PCL. Their interactions with PMMA although is not as favorable as PCL, but make them a relatively good candidate to dissolve PMMA. The favorable interaction of PCL with DCM and THF increases the amount of PMMA in PCL-rich phase which is followed by reducing PCL heat of fusion in this phase (Table I).

Furthermore, in the case of rPMMATOL, incompatibility between PMMA and TOL concluded from solubility parameters, causes to increase the free energy of rPMMATOL sample. Introducing more amount of PCL as a component which benefits from relatively more favorable interaction with dominant component, TOL, causes the free energy of the system to reduce. This thermodynamic force increases the PCL concentration in PMMA-rich phase in which it confirms by higher value of heat of fusion associated with PCL crystals in this sample (Table II and Figure 4). Therefore, TOL can be considered as a solvent with higher power to induce PCL/PMMA miscibility in PMMA-rich phase. Such phenomena cannot be occurred for samples prepared from DCM and THF. Strictly speaking, it can be concluded that interaction of solvent with individual polymers plays the dominant role to induce miscibility. This finding is in a good agreement with those claimed by Zeman and Patterson [10].

IV. CONCLUSION

The influence of solvent on the miscibility behavior of PMMA/PCL blend was investigated using three different solvents, i.e. THF, Toluene and DCM by thermal analysis approach. It was concluded that the solvent plays a prominent role in miscibility of this blend which can be also described by Hansen solubility parameter. Thermal events of PCL and PMMA in pure and mixed state such as enthalpy of melting as well as glass transition were determined. Among used solvent, DCM was established as solvent with highest induced miscibility in PCL-rich phase. In the case of PMMA-rich phase, TOL created the highest miscibility. Therefore, it could be said that the solvent-induced miscibility is not only affected by solvent-polymer interaction but also depends on the polymer concentration in each phases. As a consequence, it can be figured out that enthalpies of PCL in the PCL/PMMA solution blend result in a series of decreasing solvent power to mix of two incompatible polymers (PMMA and PCL) in PCL-rich phase according to DCM>THF>TOL. While, these enthalpies result in a series of decreasing solvent power in PMMA-rich phase according to TOL>THF>DCM.

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