

Dynamic Copolymerization of Butyl Acrylate with Diallyl Phthalate in Poly(Methyl Methacrylate) Matrix

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This work describes the way of preparation of polymer blends by polymerization (PBA-co-DAP) in melt of PMMA under intensive stirring. The original macromolecular network is exposed to shear stress. When critical deformation force is exceeded, the network begins to rupture. It is assumed that microgels appear also due to coalescence P(BAC-co-DAP) molecules and due to their crosslinking during the synthesis. The foils of PMMA blend containing 19.9 mass % of P(BAC-co-DAP) should be of fourteen-times increased non-notches impact resistance in comparison with foils of original PMMA. The influence of shear tension on the course of polymerization and properties of the prepared blends has been followed with the help of torque of kneaders in the reactor.

The increase of toughness of fragile polymers is most successfully reached by dispersion of rubber particles in polymer matrix. Optimal size of modifier particles, low interphase energy, and good adhesion to matrix of modified polymer are relevant requirements for an efficient increase of toughness of mixed polymer material. Dispersed rubber particles function as tension concentrators facilitating dissipation of impact energy. The second phase is characterized by spheric particles of the diameter of 0.1 to 5 μm created under dispersion; their amount in blend represents most commonly 0.1 up to 0.2 of volume fraction [1, 2]. As rubber additives for transparent polymer matrixes (organic glasses) polyacrylates and polymethacrylates with low values of T_g transition and close values of interaction parameters are added [3]. With such combination we necessarily have to avoid dissolving of elastomer component in the matrix to prevent formation of a single-phase system.

The solubility of modifier in matrix results in the fact that the tough fracture of the material is reached at the expense of yield stress, decrease of modulus, and decrease of T_g temperature. Similar influence on the properties is followed when statistic copolymer is prepared from monomers which are components of the polymers of the system. In multiphase polymer systems the increase of toughness is not accompanied by the above negative effect of the added polymer on the matrix. On the contrary, we observe considerable increase of fraction energy and impact toughness under maintaining other physical and mechanical properties of the matrix [2].

Maintaining the two-phase system in polymer blends with soluble components is often solved by crosslinking in elastomer phase. With respect to the required size of elastomer heterogeneities the task

is to create microgels. A well-tried method of preparation of particle polymer is emulsion polymerization [4]. This is the way how to prepare submicrometric homogeneous polymer particles or particles containing several layers. Yet, there is a disadvantage to separate the synthesis of particle modifier which is a necessity of its additional dispersion in the matrix. One has to notice also the fact that during isolation of polymer aggregates of big size and changed structure are formed [5]. This is why some cases of synthesis of microgel elastomer particles right in the matrix of modified polymer are preferred (similar to the dynamic vulcanization of rubbers [6, 7]).

Such procedure was used to increase impact resistance of poly(methyl methacrylate) (PMMA) utilized for an injection moulding. The process of synthesis and the preliminary results of evaluation of prepared blends are mentioned in the work. PMMA matrix was modified mainly by poly(butyl acrylate) (PBAC) containing also diallyl phthalate (DAP) and peroxide initiator.

EXPERIMENTAL

Impact resistance of PMMA was improved in mixing chamber of plastograph Plasti-Corder Brabender. We did not make any arrangement to maintain atmosphere free of oxygen. Microgel heterogeneities were prepared by polymerization of butyl acrylate (BAC) with crosslinking comonomer diallyl phthalate in the melt of PMMA under simultaneous effect of shear tension. Batch for modification was prepared by spreading of monomers with initiator on beads of suspension PMMA 150 min before the beginning of polymerization. The course of reaction was followed

according to the change of torque of kneaders in mixing chamber of plastograph.

The temperature of heating medium was 403 K and 423 K, and the turning frequency of mixing blades was 25 min^{-1} .

Before starting the polymerization, monomer BAC was distilled under lowered pressure of nitrogen. The inhibitor of polymerization was removed by the usual way in advance [8].

Diallyl phthalate was used without any preliminary treatment, *i.e.* such as it is supplied by Fluka. Also peroxides, *t*-butyl perbenzoate (*t*-BPB) and dicumyl peroxide (DCP) came from the same supplier.

Other utilized solvents and reagents were of anal. grade.

Insoluble part of samples and degree of crosslinking were determined after dissolving the polymer blend in toluene at 298 K after 5 d. The solution was changed for three times to remove soluble part of the sample. Testing bars were prepared in a plate press at 493 K and under pressure of 3 kPa. The particles were taken out of the press after cooling under 373 K and their size was $50 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$.

The impact resistance was determined with the help of the method of the falling weight and noninstrumented equipment. This method is useful for thin samples [2]. The impact rate was 2.5 m s^{-1}

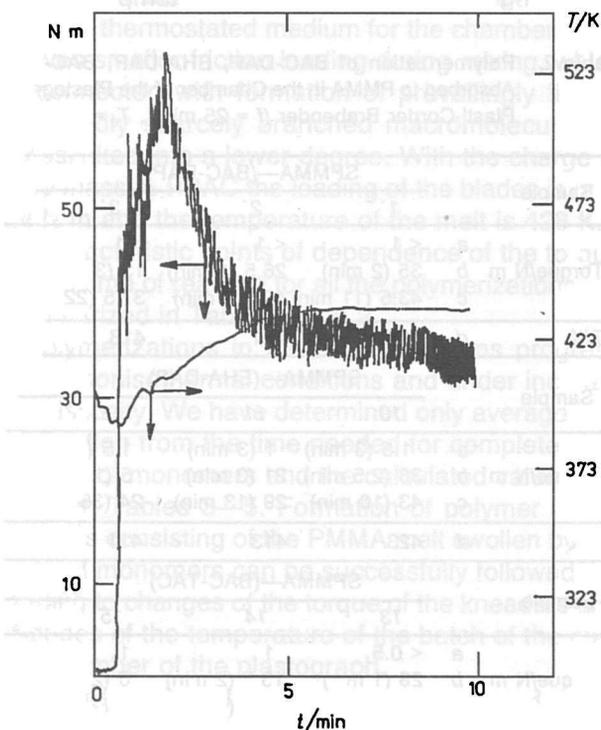


Fig. 1. The course of temperature and torque of blades in the chamber of the plastograph Plasti-Corder Brabender during stirring of PMMA beads at $f = 25 \text{ min}^{-1}$, heating medium, temperature 423 K.

and the resistance is presented as an energy needed for breaking the bars (average of two measurements).

RESULTS AND DISCUSSION

For synthesis we have chosen compromise conditions so that the reaction progressed under sufficiently high shear tension and low turning frequency of mixing blades. Also with respect to the boiling point of the utilized monomer BAC, polymerizations in mixing chamber were carried out at temperatures just slightly higher than T_g of PMMA.

The course of torque was at first followed for the melt of PMMA matrix alone. At 388 K the bead polymer remains loose. After increasing the temperature to 413 K, a homogeneous melt aroused in the chamber, with the viscosity following the course of torque recorded in Fig. 1. Initial loading of the blades caused by gradual filling the chamber with cool PMMA beads, decreases as the temperature of the melt is increased and the chamber is being filled. After 8 min, the temperature is settled at 433 K (10 K higher than the heating medium) and the torque at 33 N m.

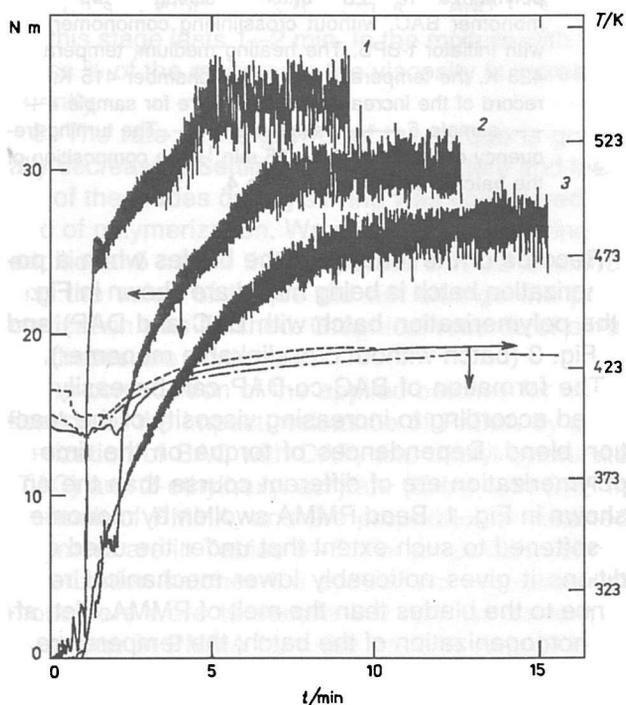


Fig. 2. The course of temperature and torque of blades in the chamber of the plastograph Plasti-Corder Brabender at polymerization of 25 g batch consisting of PMMA and monomers BAC and DAP and initiator *t*-BPB. The heating medium, temperature 415 K. The record of the increase of temperature for sample 1 - - - -, sample 2 —, sample 3 — · — ·. The turning frequency of the blades: $f = 25 \text{ min}^{-1}$. The composition of the batches is shown in Table 3.

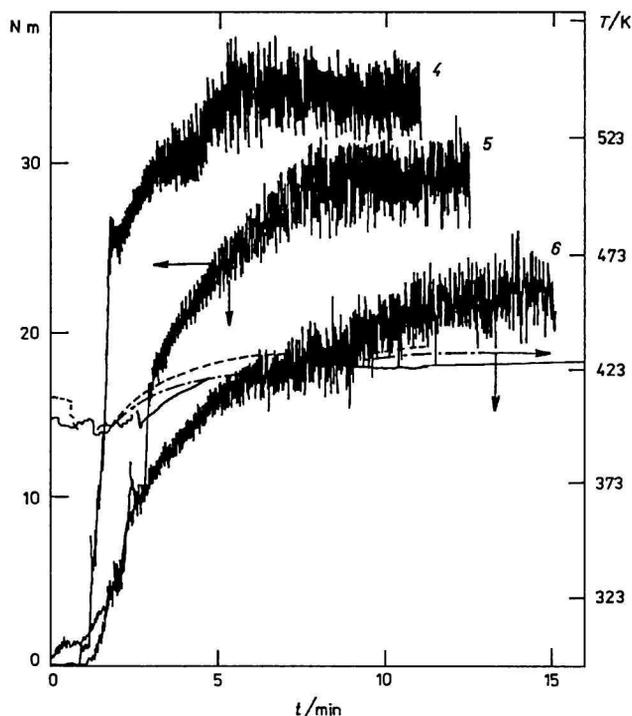


Fig. 3. The course of temperature and torque of blades in the chamber of the plastograph Plasti-Corder Brabender at polymerization of 25 g batch consisting of PMMA with monomer BAC, without crosslinking comonomer and with initiator t-BPB. The heating medium, temperature 423 K, the temperature of empty chamber 415 K. The record of the increase of temperature for sample 4 — —, sample 5 ———, sample 6 —·—·—. The turning frequency of the blades: $f = 25 \text{ min}^{-1}$. The composition of the batches is shown in Table 4.

Records of the loading of the blades when a polymerization batch is being mixed are shown in Fig. 2 (the polymerization batch with BAC and DAP) and in Fig. 3 (batch without crosslinkable monomer).

The formation of BAC-co-DAP can be easily followed according to increasing viscosity of the reaction blend. Dependences of torque on the time of polymerization are of different course than the one shown in Fig. 1. Bead PMMA swollen by monomers is softened to such extent that under the used conditions it gives noticeably lower mechanical resistance to the blades than the melt of PMMA. Yet, after homogenization of the batch, the temperature in the chamber begins to rise fluently, and the torque is increased simultaneously. This suggests an increase of the viscosity of the system as a result of polymerization of added monomers. For a batch with 6.9 mass % of monomer the torque is settled at 34 N m, that is 1 N m higher than the one followed in the melt of PMMA. Under increased content of the elastomer component in the blend (11.9 mass % and 19.9 mass % P(BAC-co-DAP)) the loading of the blades was lowered to 30 N m, resp. 26.5 N m. It was reflected by slight decrease of temperature of

Table 1. Polymerization of BAC-DAP Absorbed to PMMA in the Chamber of the Plastograph Plasti-Corder Brabender ($f = 25 \text{ min}^{-1}$, $T_0 = 415 \text{ K}$)

Sample	t-BPB		
	1	2	3
Torque/N m	a < 0.5 b 25 (1 min) c 34 (4 min)	< 0.5 15 (2 min) 30 (6 min)	< 0.5 10 (2 min) 26.5 (10 min)
T/K	d 433	433	431

Sample	t-BPB, without DAP		
	4	5	6
Torque/N m	a < 0.5 b 25 (1 min) c 33.5 (6 min)	< 0.5 16 (2 min) 29 (9 min)	< 0.5 8 (2 min) 22.5 (14.5 min)
T/K	d 433	431	428

Sample	DKP		
	7	8	9
Torque/N m	a 0.5 b 29.5 (2 min) c 35.5 (5 min)	0.5 20 (3 min) 31 (9 min)	0.5 10 (3 min) 26 (15 min)
T/K	d 435	433	429

a) Batch at introduction; b) after the beginning of polymerization; c) steady state — the end of reaction (the time of polymerization); d) the temperature in the chamber after the end of polymerization.

the melt. Yet, the heat released by shear stress keeps the temperature 8 K above the temperature of heating bath and 16 K above the temperature of

Table 2. Polymerization of BAC-DAP, EHA-DAP, BAC-TAC Absorbed to PMMA in the Chamber of the Plastograph Plasti-Corder Brabender ($f = 25 \text{ min}^{-1}$, $T_0 = 393 \text{ K}$)

Sample	SPMMA—(BAC-DAP)		
	1'	2'	3'
Torque/N m	a < 1 b 35 (2 min) c 43.5 (11 min)	< 1 26.5 (1 min) 40 (16 min)	< 1 13 (3 min) 37.5 (22 min)
T/K	d 425	421	418

Sample	SPMMA—(EHA-DAP)		
	10	11	12
Torque/N m	a 1.5 (3 min) b 38 (2.5 min) c 43 (10 min)	1 (3 min) 21 (3 min) 29 (13 min)	1.5 (1.5 min) 5 (1.5 min) 24 (35 min)
T/K	d 423	413	411

Sample	SPMMA—(BAC-TAC)		
	13	14	15
Torque/N m	a < 0.5 b 28 (1 min) c 35 (10 min)	1 13.5 (2 min) 31.5 (16 min)	1 6 (2 min) 33 (27 min)
T/K	d 413	413	415

a) Batch at introduction; b) after the beginning of polymerization; c) steady state — the end of reaction (the time of polymerization); d) the temperature in the chamber after the end of polymerization.

Table 3. Polymerization of BAC-DAP in the Reaction Mixture with PMMA in the Chamber of the Plastograph Plasti-Corder Brabender. a) The Properties of the Composites PMMA—P(BAC-co-DAP)

Sample	1	2	3	1'	2'	3'
PMMA	93.0	88.0	80.0	93.0	88.0	80.0
w(BAC)/%	6.5	11.2	18.9	6.5	11.2	18.9
DAP	0.4	0.7	1.0	0.4	0.7	1.0
Initiator		t-BPB = 0.1			t-BPB = 0.1	
T/K^b	398	398	398	393	393	393
	433	433	431	425	421	418
$R_p/(g\ dm^{-3}\ min^{-1})^c$	17.5	20	20	6.7	8	9.1
w(Gel)/%	33	40	10	62	39	15
Degree of swelling ^d	3	3	25	2	3	17
Impact resistance ^e kJ m ⁻²	3.4	4.3	21.4	8	28.6	34.2

a) Monomers were allowed to swell PMMA for 90 min before filling the chamber. Turning frequency of blades was 25 min⁻¹, temperature of heating medium was 423 K (samples 1—3) and 403 K (samples 1'—3'). The batch was 25 g. b) Nonisothermal polymerization with fluent increase of the temperature in the marked interval (Figs. 2 and 3). c) R_p means the average rate of polymerization. d) Mass ratio of wet to dry gel after swelling in toluene at 298 K. e) PMMA evaluated in the same way was of the impact resistance 2.4 kJ m⁻².

empty chamber before filling by polymerization charge.

The proceeding reactions of branching and crosslinking of macromolecules raising by DAP copolymerization were also reflected in records of torque. In batches for polymerization without crosslinkable comonomer the melt in a steady state has lower torque (Figs. 2 and 3), which corresponds to smaller difference of temperature between the melt and the thermostated medium for the chamber. That proves smaller friction loading during mixing, which is connected with formation of prevalingly linear, admittedly scarcely branched macromolecules or crosslinked into a lower degree. With the charge of 19.9 mass % PBAC the loading of the blades is only 22 N m and the temperature of the melt is 428 K.

Characteristic points of dependence of the torque on the time of reaction for all the polymerizations are summarized in Tables 1 and 2.

Polymerizations in the above systems progress under nonisothermal conditions and under increasing viscosity. We have determined only average rate of reaction from the time needed for complete conversion of monomers and the calculated values are listed in Tables 3—5. Formation of polymer in the systems consisting of the PMMA melt swollen by the applied monomers can be successfully followed according to changes of the torque of the kneaders and changes of the temperature of the batch of the mixing chamber of the plastograph.

Polymerization of batches with marks 1—3 at the temperature of chamber 415 K (Fig. 2) can be described as follows:

1. Heating of the charge for 2 min at almost negligible torque to 1 N m. The temperature sensor records the decrease of temperature to 393 K.

2. Yet, in this phase there is a simultaneous start of the polymerization, which causes the increase of viscosity of the environment with gradual increase of the temperature of the melt. For the applied amounts of monomers 6.9 mass % and 11.9 mass %, this stage lasts 1—2 min. In the mixture with 19.9 mass % of the monomers the viscosity is increased fluently.

3. The rate of the growth of the torque is gradually decreased. Settling of the temperature and loading of the blades during stirring was considered the end of polymerization. We continued the stirring for additional 5 min. If the temperature in the chamber and the value of torque did not change the polymerization was finished. Graphical records of other syntheses are analogous.

The composition of the applied batches for modification of the impact resistance of PMMA by polymerization of BAC with DAP, and triallyl cyanurate (TAC) and 2-ethylhexyl acrylate (EHA) with DAP in the melt of PMMA, and the properties of obtained polymers are in Tables 3—5. For preparation of polymerization batches the applied concentrations of monomers were to secure the optimal content of elastomer in PMMA from the point of view of influencing the impact resistance [2]. This is based on the assumption of full conversion of the monomers.

The results given in the tables show that by the polymerization of BAC component with crosslinking comonomer DAP in the melt of PMMA one can obtain a composite with the increased impact resistance. A comparison of values in columns 1—3 and columns 1'—3' in Table 3 suggests that besides concentration of the elastomer, the value of the impact resistance of the final material is influenced by the temperature of polymerization. Polymer blend

prepared at lower temperature 393 K has higher resistance against damage by knock in comparison with samples polymerized at higher temperature 415 K. This can be due to the higher viscosity of the system, and thus also to increased shear stress of polymer and formation of more suitable structure of elastomer microparticles. After polymerization of the same blends at higher temperature the torque of mixing blades of the plastograph was by 10 N m lower (Tables 1 and 2).

The decrease of the amount of insoluble part in samples with higher content of BAC was unexpected. One of the possible explanations is that due to the effect of stirring the new macronetwork is changed into microgel particles which are soluble in toluene. This idea is supported by the fact that the samples exhibit the highest values of impact resistance while in the sample 6 without crosslinking comonomer DAP (Table 3), which is completely soluble, such increase of impact resistance was not observed.

The amount of insoluble polymer exceeding the amount of the added monomers points out a considerable degree of entangling of chains of P(BAC-co-DAP) with PMMA macromolecules. This phenomenon is much pronounced namely at low concentrations of monomers. The plausible explanation can be found in different structures of formed crosslinked polymer. At the low amount of BAC in a batch the branching in growing macromolecules prevails or only slightly crosslinked network is formed. Higher concentrations of BAC and DAP in the PMMA melt prefer crosslinking and coalescence of discrete macromolecules in microgel particles. As opposed to the high amount of BAC-co-DAP in the blend, the number of accessible free ends of the network for entanglement with PMMA is lower. This explanation corresponds to the present opinion about function

of rubber polymers for increasing of toughness of amorphous thermoplastic polymers [2]. Without crosslinking comonomer, PBAC itself influences the impact resistance of prepared samples in essentially smaller extent.

The presence of toluene-insoluble part also in the blends not containing DAP can be caused by peroxidic crosslinking of PBAC through the alkyl chain of the ester [9]. Yet, also in this case at 6.5 mass % PBAC in the polymer blend the insoluble part is higher than at 11.2 mass % PBAC.

In one series the elastomer component P(BAC-co-DAP) was replaced by EHA; in other syntheses we used trifunctional TAC as a crosslinking copolymer for BAC (Table 5). The same polymerization conditions as the ones used for blends PMMA—(BAC-co-DAP) did not lead to hopeful result. After the polymerization the melts were of essentially lower viscosity at medium or higher concentrations of EHA in the batches. This was revealed also by the release of lower friction heat and the melt of the polymers in the chamber was heated less. Also the content of the gel was low (less than 10 mass %) and was of low density of crosslinks. The impact resistance is very close to the one determined for the initial PMMA.

After replacement of the crosslinking comonomer by TAC, the copolymerization with BAC in the melt of PMMA progresses in the same speed as the one with DAP. Yet, the torque during stirring is lower and almost independent of the concentration of BAC. The values of the impact resistance correspond to the original PMMA polymer.

Utilization of equivalent concentration of dicumyl peroxide at temperature 423 K (Table 4, samples 7–9) resulted in a prolonging of the polymerization. The prepared PMMA composition does not differ signifi-

Table 4. Polymerization of BAC-DAP in the Reaction Mixture with PMMA in the Chamber of the Plastograph Plasti-Corder Brabender. a) The Properties of the Composites PMMA—P(BAC-co-DAP)

Sample	4	5	6	7	8	9
PMMA	93.4	88.7	81.0	93.0	88.0	80.0
w(BAC)/%	6.5	11.2	18.9	6.5	11.2	18.9
DAP	0	0	0	0.4	0.7	1.0
Initiator	t-BPB = 0.1			DCP = 0.14		
<i>T/K</i> ^b	398 433	398 431	398 428	398 435	398 433	398 429
<i>R_p</i> /(g dm ⁻³ min ⁻¹) ^c	11.0	12.6	13.1	14	13.3	13.3
w(Gel)/%	38	12	0	61	43	11
Degree of swelling ^d	3	5	—	2	3	21
Impact resistance ^e kJ m ⁻²	5.5	10.1	6.1	3.7	4.0	21.6

a) Monomers were allowed to swell PMMA for 90 min before filling the chamber. Turning frequency of blades was 25 min⁻¹, temperature of heating medium was 423 K. b) Nonisothermal polymerization with fluent increase of the temperature in the marked interval (Figs. 2 and 3). c) *R_p* means the average rate of polymerization. d) Mass ratio of wet to dry gel after swelling in toluene at 298 K. e) PMMA evaluated in the same way was of the impact resistance 2.4 kJ m⁻².

Table 5. Polymerization of BAC-DAP in the Reaction Mixture with PMMA in the Chamber of the Plastograph Plasti-Corder Brabender. a) The Properties of the Composites PMMA—P(BAC-co-DAP)

Sample	EHA-DAP			BAC-TAC		
	10	11	12	13	14	15
PMMA	93.0	88.0	80.0	93.0	88.0	80.0
w(Monomer)/%	6.5	11.2	18.9	6.5	11.2	18.9
Crosslinking monomer Initiator	0.4	0.7	1.0	0.4	0.7	1.0
	t-BPB = 0.1			t-BPB = 0.1		
T/K^b	393	393	393	393	393	393
	423	413	411	413	413	415
$R_p/(g\ dm^{-3}\ min^{-1})^c$	7.0	9.2	5.7	7.0	7.5	7.4
w(Gel)/%	8	5	8	6	2	21
Degree of swelling ^d	34	54	53	51	48	43
Impact resistance ^e kJ m ⁻²	2.7	5.7	3.7	3.0	2.4	2.8

a) Monomers were allowed to swell PMMA for 90 min before filling the chamber. Turning frequency of blades was 25 min⁻¹, temperature of heating medium was 403 K. b) Nonisothermal polymerization with fluent increase of the temperature in the marked interval (Figs. 2 and 3). c) R_p means the average rate of polymerization. d) Mass ratio of wet to dry gel after swelling in toluene at 298 K. e) PMMA evaluated in the same way was of the impact resistance 2.4 kJ m⁻².

cantly from the properties of compositions made with t-BPB (Tables 1 and 3, samples 1–3).

The above way of preparation of P(BAC-co-DAP) microgels forming the component of impact-resistant blends with PMMA differs from the dynamic crosslinking of rubbers by the fact that the elastomer phase appears in the modified matrix gradually. Radical polymerization proceeds in a medium with high viscosity and under shear deformation caused by intensive stirring. Dimensions of the appearing polymer network are controlled, besides other factors, by the utilized shear stress. Besides the formation of microgel particles by scission of crosslinked P(BAC-co-DAP) there is a possibility of creation of microheterogeneities from the molecules P(BAC-co-DAP) by their coalescence. These are preferentially swollen by present monomers and gradually formed microgel particles in the PMMA matrix. We are led to this explanation by the fact that we failed to disintegrate the macronetwork P(BAC-co-DAP) prepared by separate polymerization into particles capable to create compatible polymer blend with PMMA. As opposed to this result *in situ* pre-

pared compositions form blends of increased impact resistance.

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