The synthesis of one homologous series of methacrylate monomers and their polymers was carried out to observe the dependence between the polarization and some structural aliphatic features. Investigations of the thermoanalytical, structural and pyroelectric properties of the composites were carried out. All investigated samples showed a typical non-linear behavior of the pyroelectric response under an applied electric field. The saturation voltage was around 12.5 V \text{m}^{-1} on average. By increasing the length of the aliphatic tail of the homologous series a change from antiferroelectric to ferroelectric behavior was observed. As a result of this study, we were able to control the ferroelectric or antiferroelectric properties in mixtures of achiral polymer-monomer composites taking into account the appropriate length of the aliphatic alkyl chain of the components in the mixture. © 2012 The Royal Society of Chemistry.